Dyed Wastewater Treatment via Ionic Liquids

By

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MACKEVIN LIM CHUN TECK)

ABSTRACT

Currently, Waste water generated by the textile industry is one of the main issues that contribute to the water pollution. This is due to the fact that, this type of industry consumes large amount of process water and chemicals and therefore, produces high volume of highly polluted discharged water. Due to its dreadful impacts towards the environment and aquatic livings, various researches have been conducted to treat these effluents. Presently, various methods have been established by the researchers such as the biological, chemical and physical treatment.

Associated with that, removal of dyes via ionic liquids is one of the techniques, which is still not widely applied by industries but it has been discovered to be able to treat dyed wastewaters. Since the research of ionic liquid for this application is still at surface level, the major concerns such as process efficiency in terms of economic and residual water quality and at the same time, to improve the amount of dye removal with minimal usage of ionic liquids. In this research project, experiments have to be carried out by varying few parameters, which are concentration of dyes in waste water, pH, temperature and effect of types of ionic liquids. Results from the parameters tested will be analyzed quantitatively in percentage of dye removed per unit mass of ionic liquids with the help of UV-Vis spectrophotometer.

ACKNOWLEDGEMENT

In order to succeed in completing the project, the author truly understands that this will not be possible without the involvement and contributions of certain parties, organizations and individuals. Therefore, the author would like to express his deepest gratitude

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 Background of Study

With the ever-growing of the textile & apparel manufacturing, printing, paper industries and etc, where the textile industry itself accounted for USD 385 billion of the overall global trade (EconomyWatch, 2010), there is no escape in the extensive use dyes. This resulted in high discharging rate of dyed wastewater into the environment. The dyed effluent from these industries usually remains untreated or undergoes improper treatment before being channeled to the water resources. Taking China for example, the silk production factories located in Qinghai, which is nearby the famous Yellow River have been discharging approximately 2500 tonnes per day of dyed waste water, which are mostly untreated. This consequently polluted part of the river water (which is the daily fresh water supply for the community in Qinghai) by turning the water into reddish in color due to the dye.

The figure below is the current condition of water in part of the Yellow River in Qinghai:

Figure 1.1: Pollution due to Red Dye in the Yellow River nearby Qinghai, China

Worldwide recognition through the UNESCO (United Nations Educational, Scientific, and Cultural Organization) seems to have had a significant influence on the growth of batik industry in Malaysia. Since recognized as objects of Malaysian native cultural heritage on October 2, 2010, the growth of the "batik" industry in Malaysia began significantly (Nita Kusmawati, et.al., 2012). However, except of all the positive effects arising from the development of batik industries in the homeland, tucked well as a number of problems are associated with wastewater treatment problems. Because the batik industry is one of the largest industrial water users in every step of the production process, the generated wastewater was also in large number. In the process of production, batik industry uses a lot of chemicals and water. The chemical is commonly used in dyeing process. In general, the pollutants contained in industrial waste in the form of batik are heavy metals, suspended solids, or organic substances. Therefore, if this batik wastewater flowed directly into the environment without any prior processing, it can degrade the quality of the environment and damage the life that exists in the neighborhood.

Presently, there are several technologies, which have been put into application in treating the dyed waste water, which are namely biodegradation, coagulation and flocculation, membrane adsorption and etc. In this research, liquid-liquid separation via ionic liquids has been chosen to determine the effectiveness in dyes removal from the wastewater.

1.2 Problem Statement

As there are numerous technologies available, which are presently being applied for the removal of dye from waste water, removal of such effluent via ionic liquids technology has not been widely use by many dye-consuming industries since only a few researches have been carried out to provide sufficient proof on the effectiveness as well as versatility of ionic liquids for the purpose of dye removal. In order to provide sufficient information and data to prove the advantages and suitability of ionic liquids for the removal of dye in any condition, several parameters such as temperature, pressure, pH, concentration of dye, and etc will be studied in this research as well as its effects towards the percentage removal of dye by the ionic liquids.

Apart from that, research on the recovery of ionic liquids after the removal of dyes will also be taken into account since the recovered ionic liquids can be reuse for dye removal purpose, which can prove to be economical viable for many dye consuming industries as well as reducing the potential of water pollution from the waste water treatment of these industries.

1.3 Aim and objectives

The aim in this research project is to capitalize the utilization of ionic liquids in dye removal to be investigated by taking into account on various parameters and its effects towards the removal of dye from waste water.

Objectives: The main objectives in this research are as follows:

- **i)** To study the effects of temperature of the dyed waste water towards the amount of dye removal.
- **ii)** To study the effects of pH of the dyed waste water towards the amount of dye removal.
- **iii)** To investigate the effects of phase ratio towards the ionic liquids used.
- **iv)** To investigate the effects of concentration of dye in waste water towards the amount of dye removal.

1.4 Scope of study

The scope of study will be based on the objectives mentioned and further elaborated as follows:

1) Temperature of dyed waste water produced is usually at room temperature, which is between 25-35^{o}C. Practically, the energy requirement for waste water treatment should be at minimum, which should be in the room temperature condition. However, based on the experimental results carried out by Yuan et al.(2007), the separation efficiency of the anionic dyes in waste water increases with the increase of temperature. Therefore, further investigation will be carried out for temperature between the range of 25^{o}C to 50^{o}C, at which the range are within the room temperature ionic liquids and to control water from being vaporised.

2) The pH of dyed waste water will be investigated in between the range of 3-8 as different dyes (cationic and anionic dyes) reacts variedly at certain pH value. According to Othman et al., 2011, the percentage of dye extraction for the anionic. Black B dye is highest at lower pH (pH 3-4), and decreases as the pH value increases. While according to Pandit et al.(2004), the percentage of extraction for the cationic methylene blue is greater at high pH as compared to that of lower Ph.

3) The effect of phase ratio (Vol of IL : Vol Dyed Wastewater) will be investigated in the range between 1:10 to 1:60 to determine the dye removal efficiency as well as the adsorption capacity of the dye on the ionic liquid at different volume of dyed wastewater and constant volume of ionic liquid

4) The concentration of dye to be investigated in this research is between 50-500 ppm, which is the average range of dye concentration in the waste water generated by current dye consuming industries with reference to the research of Moghaddam et al.,(2010) as well as Lee et al,(2008).

1.5 Feasibility of the Project within Scope and Time Frame

This project is expected to be finished in about 7 months. During this time, the project will consists of experimental set-up, experimentation on various parameters on the dye removal and chemical analysis after the experiment to study the composition of the components in the treated waste water. From given allocation of time and operating conditions that will be varied in the experiment, this project is expected to be completed in the time given. All the scope of study that has been mentioned also will be done during the allocation of time. The feasibility of this project is shown in the Gantt chart that will be shown in later section. From there, it shown that this project will be completed and feasible within the allocated scope and time frame.

CHAPTER 2
LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Ionic Liquid

Over the past few years, ionic liquids or specifically, room temperature ionic liquids (RTIL) have attracted much researchers attention over the past few years especially in the research of finding a ‘green’ solvent as a potential replacement for organic solvent in both laboratory as well as industrial scales of catalytic processes (Holbrey & Seddon, 1999). Even though the precise definition of ionic liquids or RTIL varies from one to the other, the main key phrase in all the definitions remains the same, which is a salt with a melting point under the temperature of $100^{o}C$ (Handy et al., 2011).

The usage of ILs in organometallic catalysis, organocatalysis and biocatalysis has also been studied and applied as they offers better selectivity, greater reaction rates, as well as having a much better catalyst or enzyme stability as compared to that of current conventional solvents (Siedlecka et al., 2011). Other areas namely, electrochemical transformation, fuel cells, solar cells, sensors, and nano-chemistry also require the application of ILs. According to Siedlecka et al., 2011 as well as Kowsari et al., 2011, due to the negligible or non-measurable vapor pressure of ILs, they can be an ideal replacement for conventional organic solvents. With the readily available range of room-temperature ionic liquids to choose from as well as its simplicity in structural modifications to the cations or changes in its anions, it provides a breakthrough to design an ionic liquid-solvent system (Kowsari et al., 2011), which can be utilized for particular processes such as waste water treatment. Therefore, there is no doubt why ionic liquids can be considered as ‘designer solvents’ with credits to the large number of cation and anion combinations whereby the ILs can possess a wide spectrum of physical and chemical properties (solubility, polarity, viscosity or solvent miscibility). Apart from application in reactions, ILs also has other environmental as well as economical benefits, which include the ability to reuse and recover the ILs, which indirectly reduces the amount of waste generated (Siedlecka et al., 2011). In terms of economical point of view, since synthesizing ILs are quite expensive, recycling the ILs after they are being regenerated will be more cost saving than having to synthesize new ILs for the same application.

The usage of ionic liquids is not limited to their application as solvents, electrolytes or catalysts.

Ionic liquids are also being used as additives, including plasticizers, components of polymer electrolytes, and porogenic agents to polymers. In recent studies, properties of polymers containing chemically bound ionic liquid are studied for any feasiblilty of their applications, which are also being explored (Kowsari et al., 2011). In this research, ionic liquids will be applied as a medium for the separation of dyes from waste water for the purpose of dyed waste water treatment for certain dye-consuming industries.

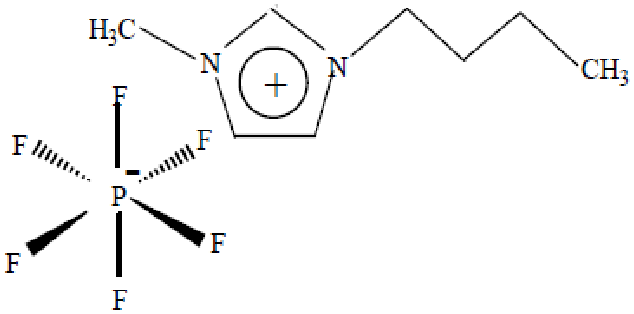
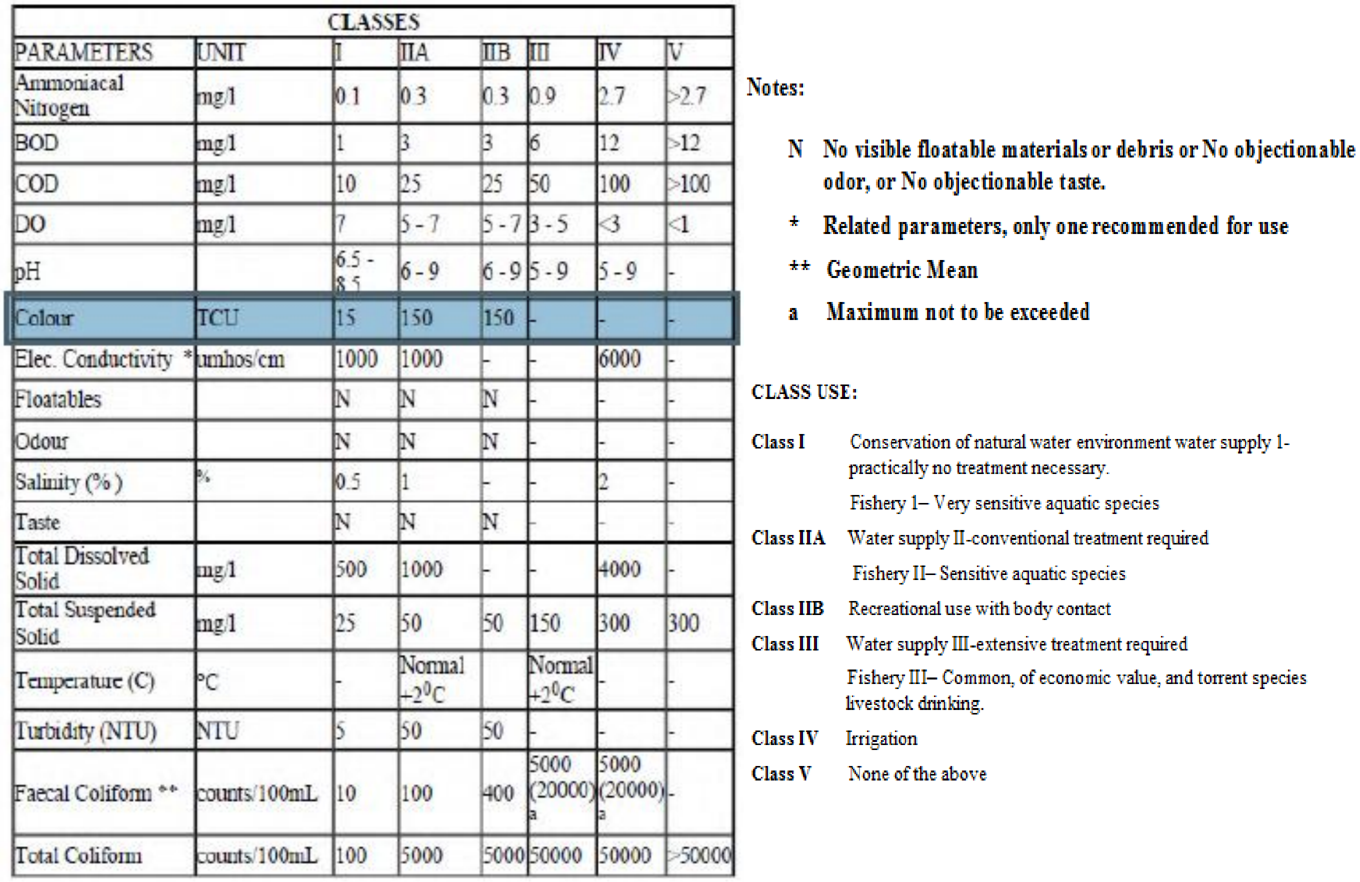


Figure 2.1.1: Chemical Structure of 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6]

2.2 Dyed Wastewater

All dye-consuming industries such as printing, textile manufacturing, apparels production, carpet manufacturing, and etc. generate effluent water, which contains multiple types of dyes. With more than 100,000 types of dyes commercially available and with over 7 x 10^5 tonnes of dyestuff produced annually (Robinson et al., 2000), discharging dyes into the water resources can cause serious environmental damage as the dye will form a color layer on the water surface, which consequently reduce the light penetration as well as the toxic/carcinogenic (Al-Degs et al, 2004) properties of some azo dyes that has the potential to endanger the aquatic ecosystems. Apart from that, waste water containing dye poses harmful threat to human lives as the dyes can contribute to certain water-borne diseases such as hemorrhage, nausea, dermatitis, ulceration of skin and mucous membranes, kidney damage, loss of bone marrow, which will lead to reduction in white blood cell and causes anemia (Pandit et al., 2004). Therefore, it is important to remove the dyes before discharging them to the environment to avoid any health hazards to human beings as well as destruction of the ecosystem. According to Othman et al., most of the synthetic dyes that is being conventionally utilized are highly soluble in water, azo-reactive dyes. Azo dyes are characterized by the existence of nitrogen to nitrogen double bonds (-N=N-) that are usually attached to two moieties that are usually belongs to the aromatic groups (benzene or naphthalene) (Rauf et al, 2012). Some example of conventional azo reactive dyes are Methyl Orange, Methyl Red, Remazol Black and etc. The reasons behind the extensive use of azo reactive dyes in most textile industries are due to the dyes characteristics of bright color, water soluble as well as its application techniques that requires low energy consumption (Asouhidou et al., 2009). According to the Interim National Water Quality Standards for Malaysia, the acceptable standard of dyes or colors in waste water that is allowed to be discharged into water resources is less than 150 TCU (True Unit Color). Below is the Water Quality Standards provided by the Department of Irrigation and Drainage Malaysia:



		CLASSES					
PARAMETERS	UNIT	I	IIA	IIB	III	IV	V
Ammoniacal Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	>2.7
BOD	mg/l	1	3	3	6	12	>12
COD	mg/l	10	25	25	50	100	>100
DO	mg/l	7	5 - 7	5 - 7	3 - 5	<3	<1
pH		6.5 - 8.5	6 - 9	6 - 9	5 - 9	5 - 9	-
Colour	TCU	15	150	150	-	-	-
Elec. Conductivity *	umhos/cm	1000	1000	-	-	6000	-
Floatables		N	N	N	-	-	-
Odour		N	N	N	-	-	-
Salinity (%)	%	0.5	1	-	-	2	-
Taste		N	N	N	-	-	-
Total Dissolved Solid	mg/l	500	1000	-	-	4000	-
Total Suspended Solid	mg/l	25	50	50	150	300	300
Temperature (C)	°C	-	Normal +2⁰C		Normal +2⁰C	-	-
Turbidity (NTU)	NTU	5	50	50	-	-	-
Faecal Coliform **	counts/100mL	10	100	400	5000 (20000)a	5000 (20000)a	-
Total Coliform	counts/100mL	100	5000	5000	50000	50000	>50000

Notes:

N No visible floatable materials or debris or No objectionable odor, or No objectionable taste.

***** Related parameters, only one recommended for use

****** Geometric Mean

a Maximum not to be exceeded

CLASS USE:

Class I	Conservation of natural water environment water supply 1-practically no treatment necessary. Fishery 1– Very sensitive aquatic species
Class IIA	Water supply II-conventional treatment required Fishery II– Sensitive aquatic species
Class IIB	Recreational use with body contact
Class III	Water supply III-extensive treatment required Fishery III– Common, of economic value, and torrent species livestock drinking.
Class IV	Irrigation
Class V	None of the above

Figure 2.2.1: Interim National Water Quality Standards for Malaysia

2.3 Current Technology in Dyed Waste Water Treatment

There are a few types of method or technology that are being applied in industries and under research for the purpose of dye removal from waste water. The followings are some of the technologies:

2.3.1 Coagulation and Flocculation

Coagulation and flocculation method is the usual techniques applied in separation of dyes from waste water or commonly, colloidal particles from the water solution. Even though the terms coagulation and flocculation are always used interchangeably, but they are both referred to two distinctive processes (Adilah et al. 2010). Particles that are smaller than approximately 10^{-5} mm may referred as colloids and particles smaller than 10^{-6} mm as solutions (Tzoupanos et al., 2008). Smaller size of particle in the dye waste water implies that the time required for settling will be greater, up to several years for certain types of dyes. Due to this, the only way for settling and the next separation is to make contacts and to form larger particles, which can be settled easier.

The first step of the process is destabilizing the particle’s charges. Coagulants of opposite charge with those of the suspended solids are added into the water and will begin neutralizing these charges. Once the charges have been neutralized, the small colloidal particles are capable of bonding together to form microflocs, which are still not visible to the naked eye. To promote better dispersion as well as contact between these particles, high energy and rapid mixing is established during this stage. After the completion of the first step, the flocculation step will take place. During this stage, the microfloc, which are formed in the preceding stage are brought into contact with each other through the slow mixing. This process will allow the growth of the floc size from microfloc to macrofloc. Formation of the macrofloc requires the sedimentation process for further removal. During this period, the produced macrofloc will settle to the bottom part of the basin. This macrofloc will form sludge with the clear wastewater after sedimentation, which requires the last process, which is filtration.

There are a few disadvantages of the coagulation and flocculation processes where the pH of the coagulants and dye wastewater mixture needs to be regulated before and after the treatment (Tzoupanos et al., 2008), which requires more consumptions of acids and caustics. Other disadvantages of this dye removal methods include sensitivity to temperature changes, the need for higher dosages because the charge neutralization is not usually sufficient, the sensitivity to the dye specific characteristics and composition, as well as the excessive sludge production, which leads to rapid exhaustion and frequent exchange of filters.

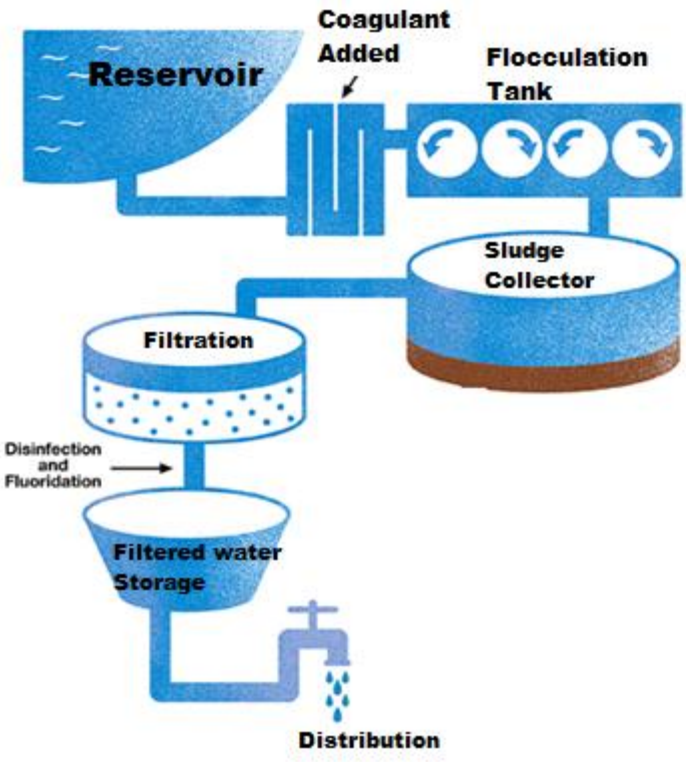


Figure 2.3.1: Example of Coagulation and flocculation methods

2.3.2 Ozonation

Ozone is a better oxidizing agent as compared to that of chlorine and hydrogen peroxide due to its instability. Oxidation by ozone has the proficiency to be used in many applications such as degradation of chlorinated hydrocarbons, phenols, pesticides and etc (Robinson et al., 2001). As for dyed wastewater, ozonation leaves the dye effluent with no colour and low COD suitable for discharge into environmental waterways (Xu and Lebrun, 1999). One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge, which will reduce the load for filtration of wastewater later. Apart from that, due to the presence of carcinogenic or toxic properties, ozonation may be used alongside a physical method to prevent this (Robinson et al., 2001).

One major disadvantage of ozonation is its short half-life, causing the efficiency of dye removal to reduce significantly at a short period of time to be in contact with the ozone. The half life is further shorten when there are presence of dye, salts, pH as well as temperature. When the condition of the dyed wastewater is in alkaline, the ozone will decompose at a faster rate. Therefore, careful and precise monitoring on the dye wastewater pH, dye concentration as well as temperature is required to ensure the half-life of the ozone is maintained as high as possible without degradation.

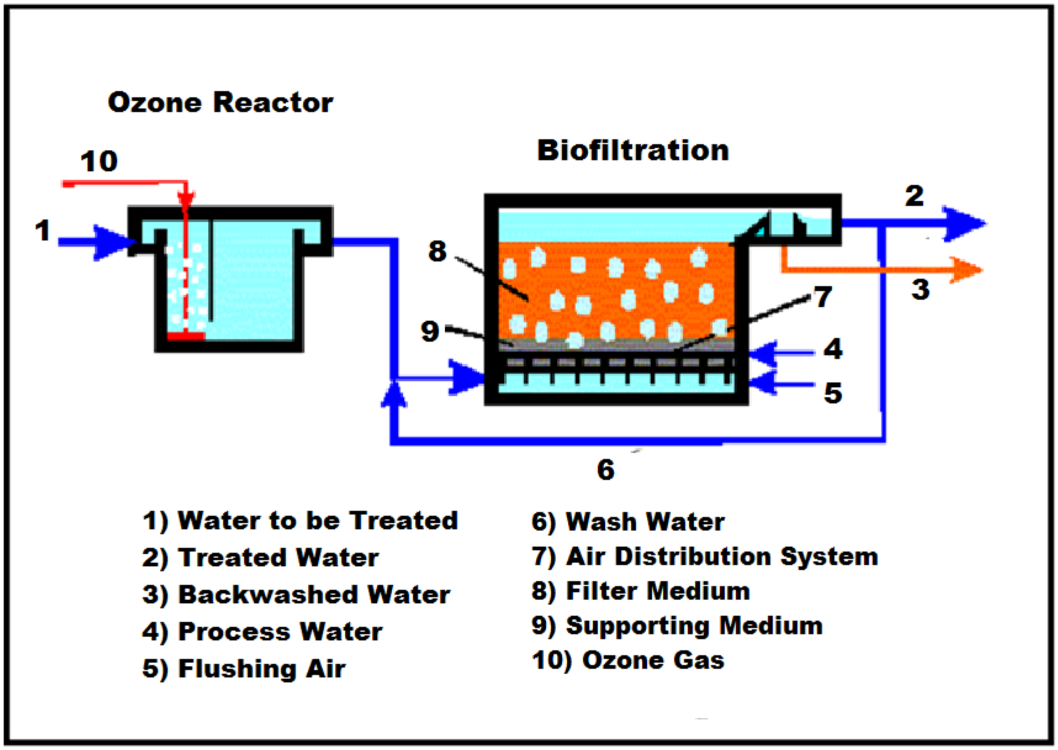


Figure 2.3.2: Example of Ozonation method

2.3.3 Decolorisation by White-rot Fungi

Utilizing white-rot fungi for is a type of biological treatment where this organisms are able to degrade lignin (Barr et al., 1994) as well as degrading dioxins and other chloro-organics. In the context of dyed wastewater treatment, the white rot fungi are able to degrade dyes by utilizing the enzymes such as lignin peroxidases (Robinson et al., 2001). Azo dyes, one of the largest class of conventional dyes cannot be degraded by other microorganisms but the dyes can be degraded by a specific species of fungus, which is P. chrysosporium (Paszczynski et al. 1995). Although white-rot fungi has the ability to decolourise dyes in liquid fermentations, the enzyme production has also been shown to be unreliable, which consequently reduce the dye removal efficiency quantitatively. This is mainly due to the unsuitable environment of liquid fermentations for enzyme production (Robinson et al., 2001). The production of enzymes were discovered to be more effective by natural fermentation of the fungi in their natural environment by having greater enzyme yield than that of liquid fermentation.

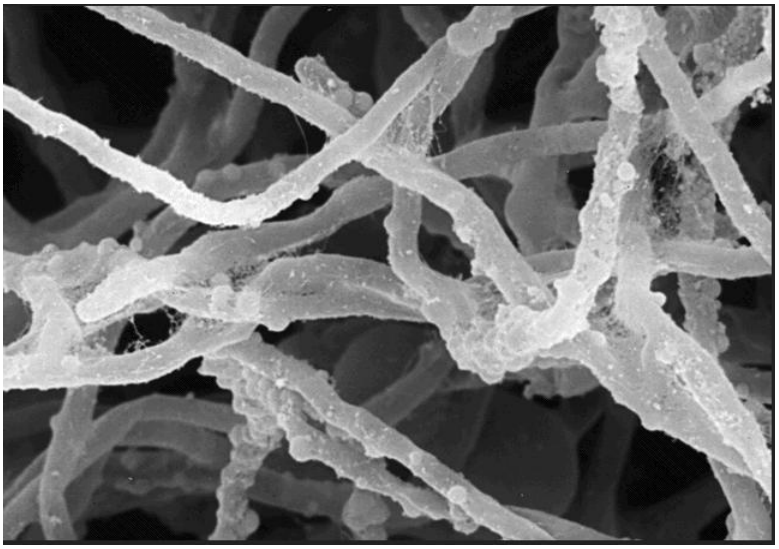


Figure 2.3.3: Example of White-rot Fungi (Phanerochete Chrysosporium***)***

Below are the chronological summary on the dyed wastewater treatment via ionic liquids:

Table 2.1: Chronological Summary of Dyed Wastewater Treatment via ionic liquids (2001-2012)

References	Affiliation	Findings
Robinson, T et al. (2001)	University of Ulster Coleraine	- Suggestion on economical altenatives for dye removal & decolorisation for different types of dye in a larger scale.

Pandit , P. and Basu, S. (2004)	IIT Delhi	- The % of dye removal varies with: - Temperature - Dye concentration - pH value of dyed wastewater - Types of dye in wastewater - Types of ionic liquids used.
All`egre, C. et al. (2005)	University of Paul C´ezanne , Paris	- Treatment of dyed wastewater and recovery of dyes through nanofiltration - Reverse osmosis processes is used to recover the dye. - The recovered dye can be reused
Othman, N et al. (2007).	UITM Johor	- The % of removal of Remazol Black B dye of textile industries varies with: 1) pH values of dyed waste water 2) Concentration of dye 3) Addition of diluents.

(Additional journal findings can be found in the Appendices)

CHAPTER 3

METHODOLOGY

3. METHODOLOGY

As this project is mainly an empirical research, the results obtained from this research can be used to compare with other literature results or results from other dye removal methods. Besides, the result obtained from this research using different configuration and the setup of the equipment in the utilization of ionic liquids to remove dye from the wastewater can be used as a basis of comparison with other researches done. The results can hence further enhance the research and development of ionic liquids for dyed wastewater treatment. The project activities in this research are mainly experimental work. After thorough literature review is done, experimental works can be conducted to investigate the 4 parameters mentioned above and the results obtained can be used to compare with that of the literature in terms of the amount of dye removed.

3.1 Experimental Procedures/Approach

The figure below shows the general experimental procedures that will be implemented in this research project.

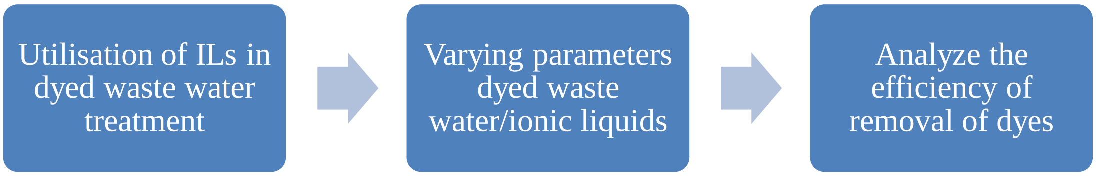


Figure 3.1.1: The schematic diagram depicting the general approach in this project

3.1.1 Raw Materials and Chemicals Required

In the experiments that are going to be conducted, several raw materials and chemicals are needed. There are:

i. Dye – Phenol Red
ii. Ionic Liquids – 1-Butyl-3-Methylimidazolium Hexafluorophosphate
iii. Acid & Caustic (H_2SO_4 & NaOH) – For regulating pH of dyed wastewater

3.1.2 Setup of Experiment

The experimental method used will be a batch method process with an adjustable rpm of the stirrer followed by a graduated cylinder for the separation of ionic liquid + dyes and water phases by gravitational force . The layout of the reactor is shown in the diagram below:

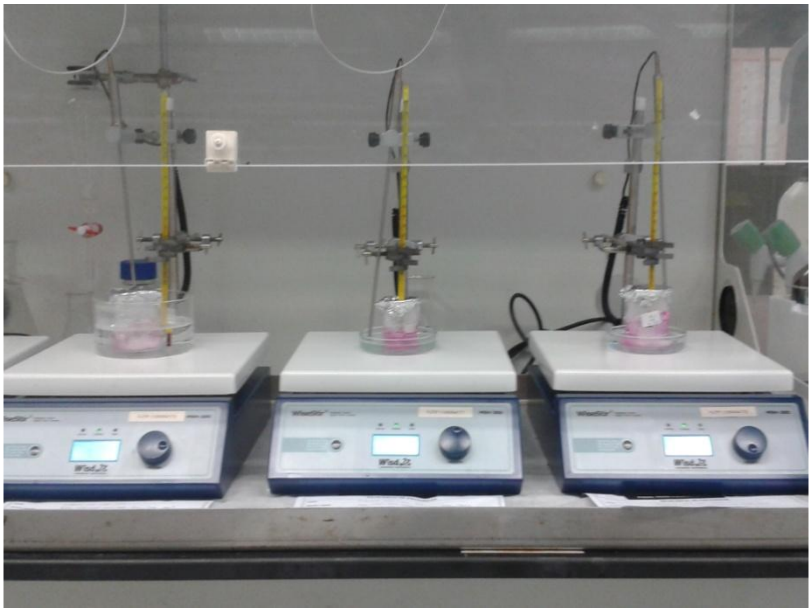


Figure 3.1.2: The schematic diagram of experimental setup for the removal of dye from wastewater

Although there are some similarities between the experimental set-up of coagulation and flocculation method and ionic liquid method for dye extraction from wastewater, there are some distinct differences. One of the differences is the separation in coagulation and flocculation method involves separation of solid and liquid phases. This is done by adding coagulants into the dyed wastewater to induce the formation of microflocs with dye in the wastewater. Since the microflocs are not dense enough and requires longer settling time to be fully separated from water, flocculation is introduced where the coagulated dyed wastewater is agitated in a flocculation tank. At this stage, microflocs will bind together to form larger macroflocs, which is denser and is able to be separated from the water with a lower settling time when it reaches the sedimentation stage.

On the other hand, separation of dye from wastewater via ionic liquid using the above experimental set-up involves separation between liquid and liquid. Presence of immiscible ionic liquid such as 1-butyl-3-methyl-imidazolium will act as a liquid adsorbent, which adsorbs the dye from the wastewater while remaining immiscible in water. Separation will occur in the separation vessel by allowing the denser water to settle forming two distinct phases. At this stage, samples are obtained from the 2 phases to perform analysis on the concentration of dye in both phases to observe the adsorption efficiency of the ionic liquid.

The above set-up can be further proved by the experiment done by Menezes, et. al, 2011. The adsorption studies for the evaluation of the Py/Si-90, Py/Si-92 and Py/Si-94 (pyridinium) ionic liquids for the removal of the RR-194 dye from aqueous solutions were carried out in triplicate using the batch contact biosorption method. For these experiments, 30.0 mg of the ionic liquids was placed in 50 mL cylindrical high-density polystyrene flasks containing 20.0 mL of dye solutions (10.00–1000.0 mg L^{-1}), which were agitated for a suitable time (0.083–24 h). Subsequently, in order to separate the ionic liquids from the aqueous solutions, the flasks were centrifuged at 12,000 rpm for 5 min The final concentrations of the dye remaining in the solution were determined by visible spectrophotometry using a T90 + UV–VIS spectrophotometer.

Experiment for the separation of dye from wastewater via ionic liquid has also been carried by Kamboh, et. al., 2010. The sorption capacity of the material 4 for RB-5 and RR-45 azo-dyes was determined by batch wise tests. Various parameters such as amount of dosage, pH, contact time and dye concentration were optimized. The experiments were conducted in 25mL Erlenmeyer flasks with glass cap which contain particular amount of the sorbents as well as particular concentration of ionic liquid solution. To obtain sorption equilibrium, the Erlenmeyer flasks were stirred on a horizontal shaker operating at a constant speed (170 rpm) at 25 ◦C for 30 min. The adsorbed dye was analyzed by the UV–Vis spectrophotometer.

3.1.3 Operating procedures for the experiment:

1) To study the effects of temperature of the dyed wastewater towards the amount of dye removal.

In the first step, volume of 15 ml of the aqueous solution (dyed wastewater) with known dye concentration (250 ppm) is added to a known volume of ionic liquid containing 1 gram of 1-Butyl-3-Methylimidazolium Hexafluorophosphate. The aqueous phase and the solvent phase are mixed thoroughly using a motorized stirrer at 800 RPM.

At the same time, the temperature of the dyed wastewater and ionic liquid mixture is then heated and maintained at a temperature of 25^{o}C. The equilibrium of the mixture observed, where there will be formation of two phases to determine the end of the stirring and heating time for the mixture.

This results in the formation of two clear liquid phases: the solvent phase containing the dye encapsulated in the reverse micelles and the clear aqueous phase. To ensure complete separation of pure phases, the two-phase dispersions are allowed to settle for 8 hours, and then the dye concentration is estimated. The samples are collected from the aqueous phase and diluted using distilled water. The diluted dye sample is analyzed in the UV-Vis Spectophotometer to determine the amount of dye separated.

The dye present in the solvent is also analyzed to check the mass balance. The concentration reading in both solvent as well as aqueous phases are recorded. The steps stating from the mixing of dyed wastewater with ionic liquids up to the analyzing steps of samples are repeated for different temperatures for 5^{o}C intervals up to 50^{o}C.

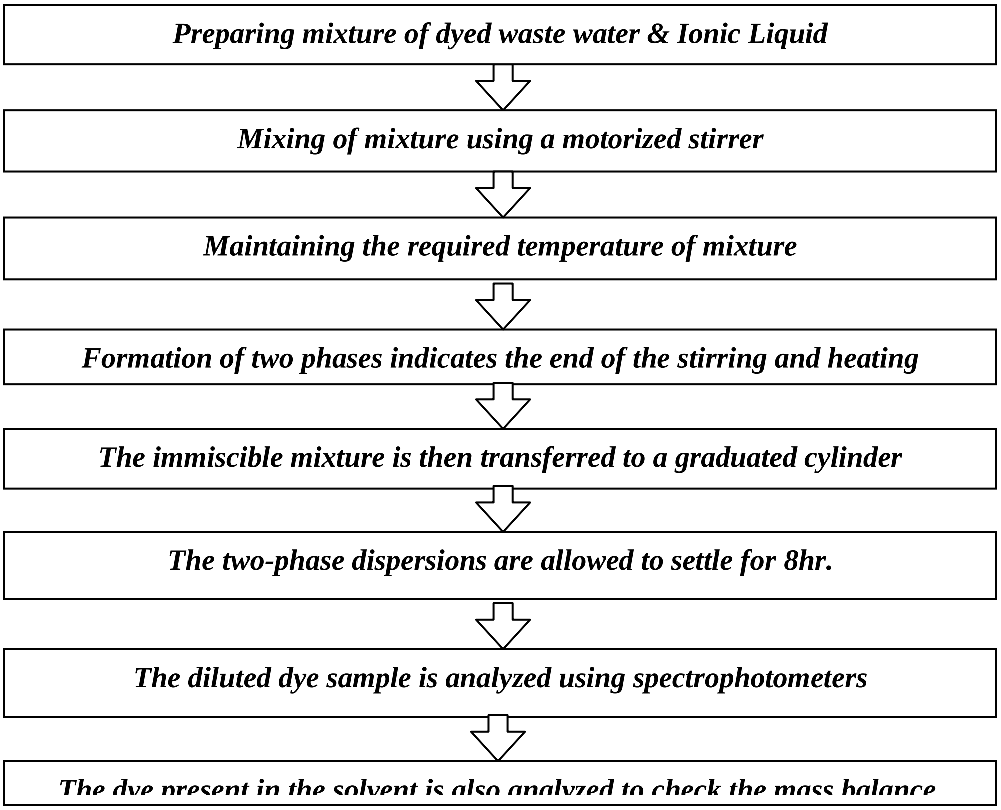


Figure 3.1.3: Flow diagram of experimental procedure (Effects of Temperature)

2) To investigate the effects of concentration of dye in wastewater towards the amount of dye removal.

In the first step, a given volume of the aqueous solution (dyed wastewater) with 250 ppm of dye concentration is added to a known volume of the solvent containing a known quantity of ionic liquid. The aqueous phase and the solvent phase are mixed thoroughly using a motorized stirrer at a fixed rpm. At the same time, the temperature of the dyed wastewater and ionic liquid mixture is then maintained at room temperature.

The equilibrium of the mixture observed, where there will be formation of two phases to determine the end of the stirring and heating time for the mixture. This results in the formation of two clear liquid phases: the solvent phase containing the dye encapsulated in the reverse micelles and the clear aqueous phase.

To ensure complete separation of pure phases, the two-phase dispersions are allowed to settle for 8 h, and then the dye concentration is estimated. The samples are collected from the aqueous phase every 1.5 hours intervals and diluted using distilled water. The diluted dye sample is analyzed in UV-Vis Spectrophotometer to determine the amount of dye separated. The dye present in the solvent is also analyzed to check the mass balance.

The concentration reading in both solvent as well as aqueous phases are recorded The steps mentioned are repeated for different concentration of dyes ranging from 250 ppm to 500 ppm with 50 ppm increment for every test.

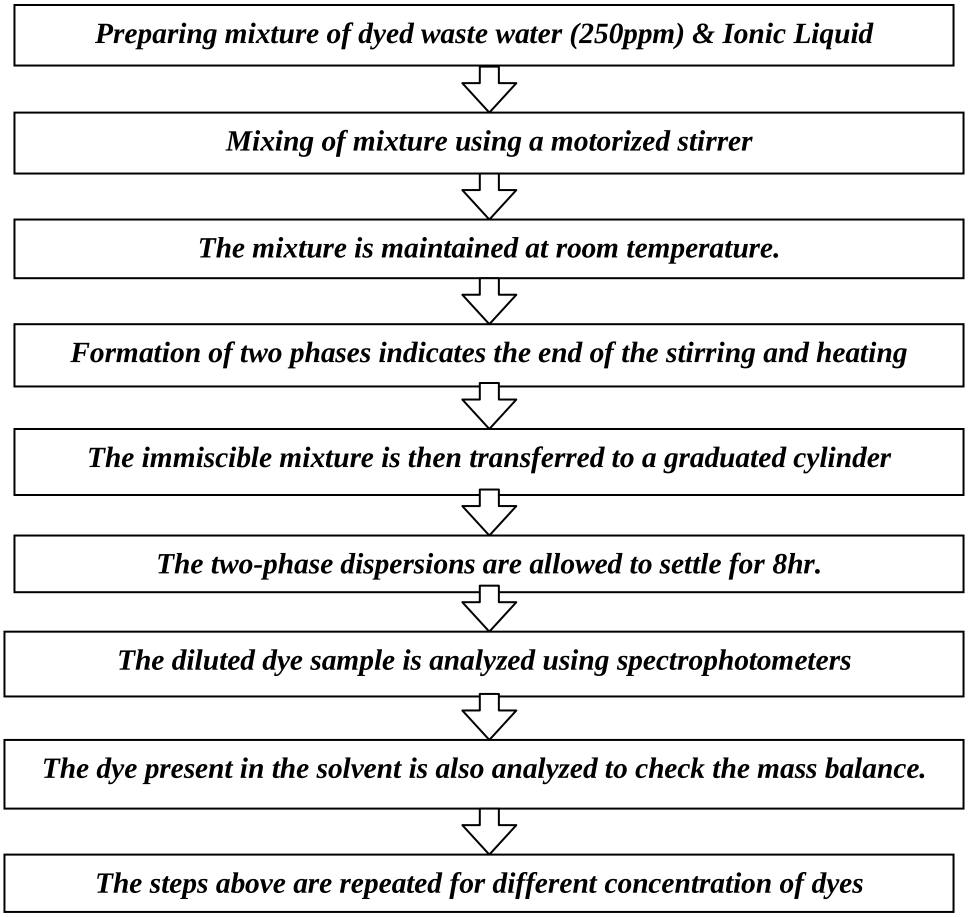


Figure 3.1.4: Flow diagram of experimental procedure (Effects of dye concentration)

3) To investigate the effects of pH of dye in wastewater towards the amount of dye removal.

In the first step, a given volume of the aqueous solution (dyed wastewater) with 250 ppm of dye concentration is added to a known volume of the solvent containing a known quantity of ionic liquid. The aqueous phase and the solvent phase are mixed thoroughly using a motorized stirrer at a fixed rpm. At the same time, the temperature of the dyed wastewater and ionic liquid mixture is then maintained at room temperature and the pH condition is set at 3.5 for this experiment by adding diluted hydrochloric acid.

The equilibrium of the mixture observed, where there will be formation of two phases to determine the end of the stirring and heating time for the mixture. This results in the formation of two clear liquid phases: the solvent phase containing the dye encapsulated in the reverse micelles and the clear aqueous phase.

To ensure complete separation of pure phases, the two-phase dispersions are allowed to settle for 8 h, and then the dye concentration is estimated. The samples are collected from the aqueous phase every 1.5 hours intervals and diluted using distilled water. The diluted dye sample is analyzed in UV-Vis Spectrophotometer to determine the amount of dye separated. The dye present in the solvent is also analyzed to check the mass balance.

The concentration reading in both solvent as well as aqueous phases are recorded The steps mentioned are repeated for different pH condition of dyed wastewater ranging from pH 3.8 to 8.5 with approximately pH 1.2 increment for every test.

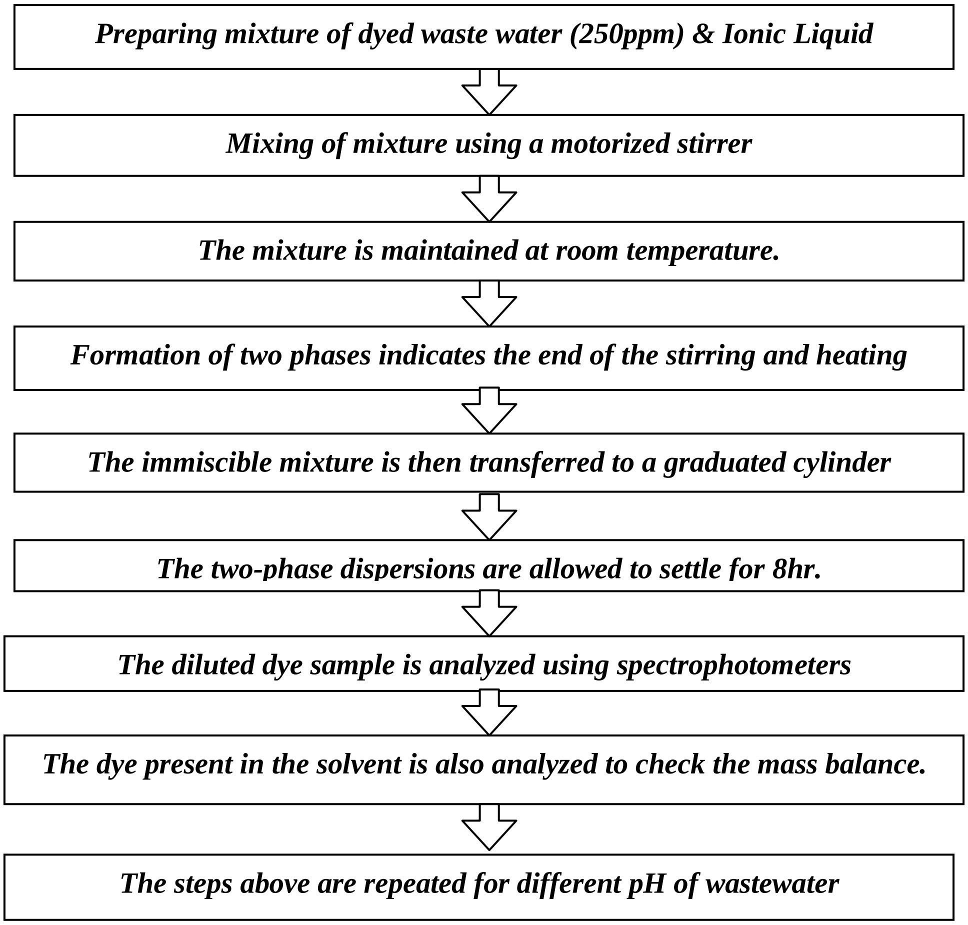


Figure 3.1.5: Flow diagram of experimental procedure (Effects of pH)

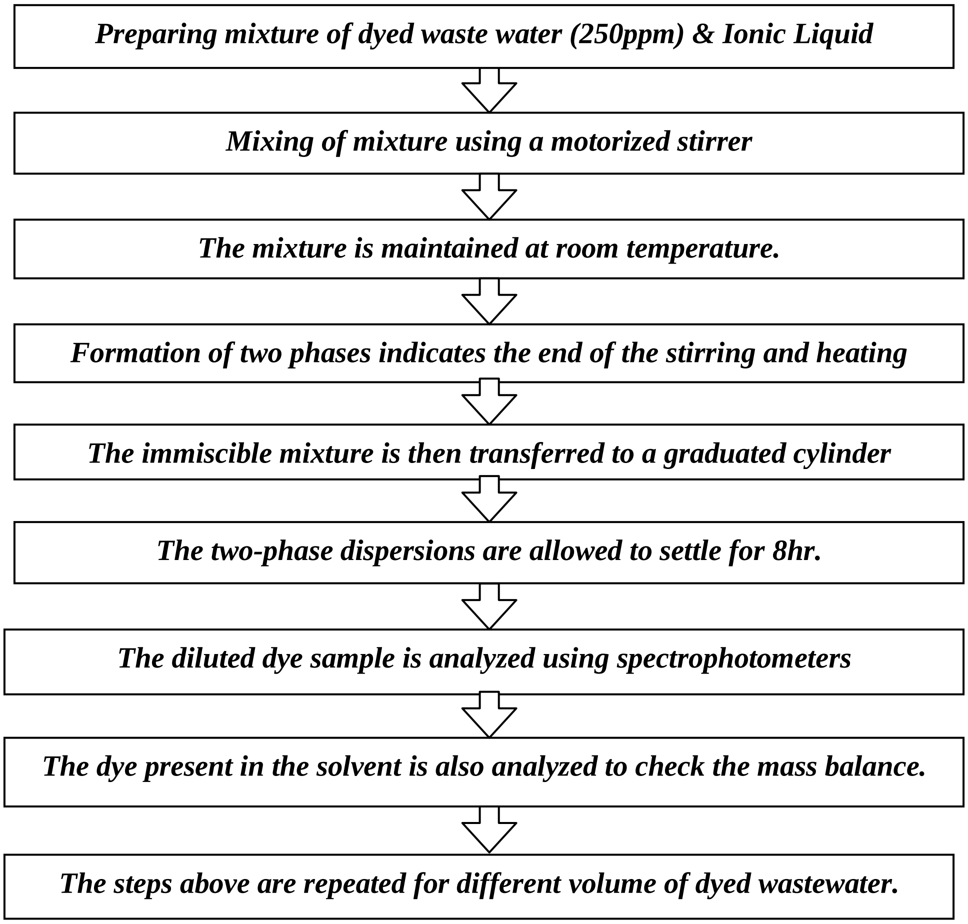
4) To investigate the effects of phase ratio of dyed wastewater towards the amount of dye removal.

In the first step, different volume of the aqueous solution (dyed wastewater) with 250 ppm of dye concentration is added to a known volume of the solvent containing a known quantity of ionic liquid. The aqueous phase and the solvent phase are mixed thoroughly using a motorized stirrer at a fixed rpm. At the same time, the temperature of the dyed wastewater and ionic liquid mixture is then maintained at room temperature.

The equilibrium of the mixture observed, where there will be formation of two phases to determine the end of the stirring and heating time for the mixture. This result in the formation of two clear liquid phases: the solvent phase containing the dye encapsulated in the reverse micelles and the clear aqueous phase.

To ensure complete separation of pure phases, the two-phase dispersions are allowed to settle for 8 h, and then the dye concentration is estimated. The samples are collected from the aqueous phase every 3 hours intervals and diluted using distilled water. The diluted dye sample is analyzed in UV-Vis Spectrophotometer to determine the amount of dye separated. The dye present in the solvent is also analyzed to check the mass balance.

The concentration reading in both solvent as well as aqueous phases are recorded The steps mentioned are repeated for volume of dyed wastewater ranging from 10 ml to 60 ml with 10 ml increment for every test.



Preparing mixture of dyed waste water (250ppm) & Ionic Liquid

Mixing of mixture using a motorized stirrer

The mixture is maintained at room temperature.

Formation of two phases indicates the end of the stirring and heating

The immiscible mixture is then transferred to a graduated cylinder

The two-phase dispersions are allowed to settle for 8hr.

The diluted dye sample is analyzed using spectrophotometers

The dye present in the solvent is also analyzed to check the mass balance.

The steps above are repeated for different volume of dyed wastewater.

Figure 3.1.6: Flow diagram of experimental procedure (Effects of Phase Ratio)

Before the samples can be analysed, a standard calibration plot must be produced beforehand. To produce the standard calibration plot, samples of known concentration are prepared as the figure below.

Figure 3.1.7: Phenol Dye Samples of Known Concentration

The samples of known concentration are then analysed with the UV-Vis Spectrophotometer to obtain the absorbance. Absorbance of a particular concentration has a distinctive peak produced at the same region of wavelength. Figure below shows the peaks produced for different concentration.

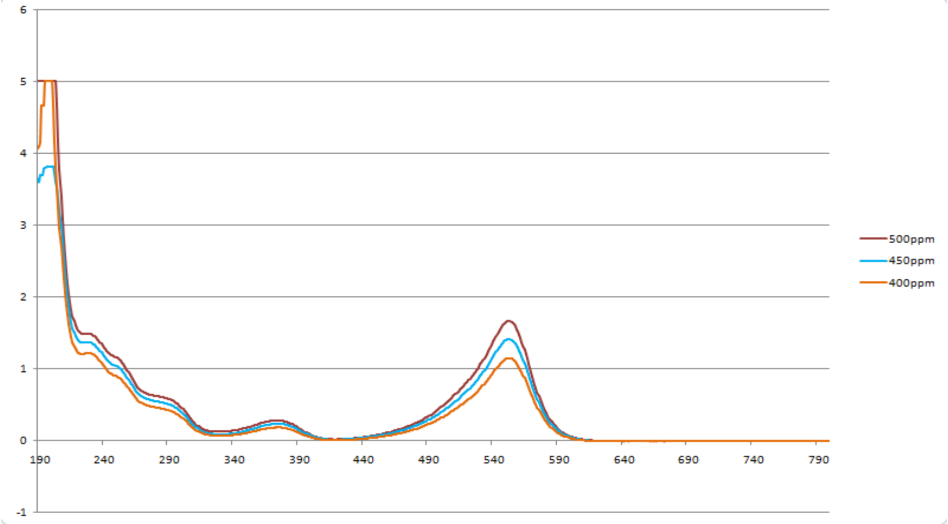


Figure 3.1.8: Absorbance vs Wavelength Graph Produced by UV-Vis Spectrophotometer at Varied Concentration

By identifying the absorbance for each known concentration, a standard calibration curve of Absorbance versus Concentration can be drawn, which adheres to the Beer's Law Equation as shown below:

Absorbance, A= **ε b c**

ε = Molar absorptivity

b = Path length

c = Concentration

Table 3.1.1: Standard Calibration Curve

Concentration (ppm)	Absorbance
500	1.86
450	1.609
400	1.343
350	1.134
300	0.95
250	0.734
200	0.543
150	0.381
100	0.285
50	0.039
10	0.011
0	0

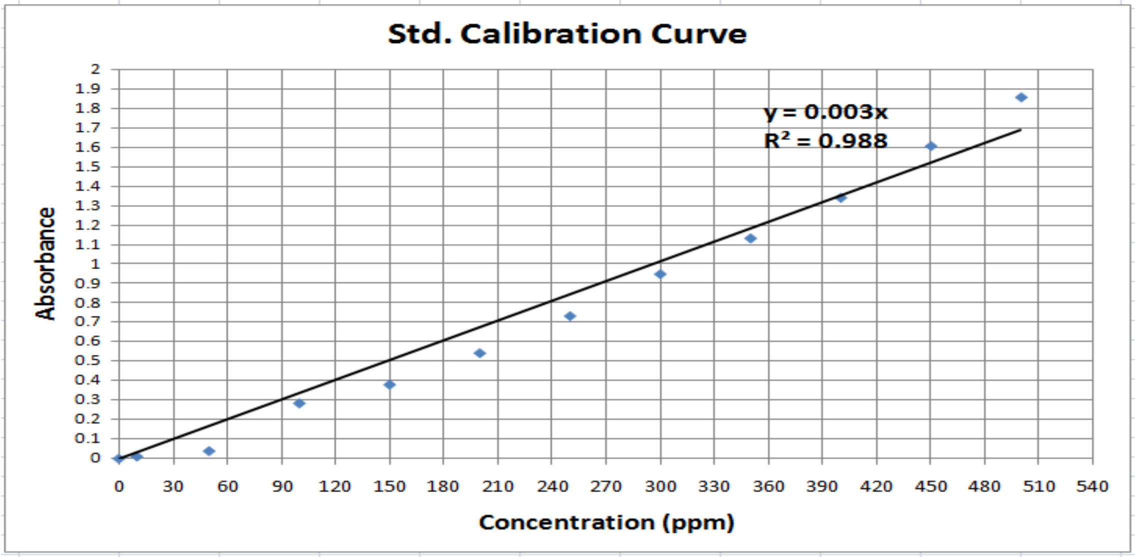


Figure 3.1.9: Standard Calibration Curve

CHAPTER 4

RESULTS AND DISCUSSION

4. RESULTS AND DISCUSSION

In Chapter 4, the results obtained from the performed experiments in relation to the dye wastewater treatment via ionic liquid are presented. The presented results are also being discussed accordingly into four main sections, namely “The Effects of Initial Dye Concentration in Dye Removal” are discussed in Section 4.1. “The Effects of Temperature in Dye Removal” are also being discussed in the latter section, which is Section 4.2; followed by Section 4.3, which is “The Effects of Phase Ratio in Dye Removal”. Lastly, “The Effects of pH in Dye Removal” in Section 4.4. Besides presenting the results and discussing on the aforementioned four parameters, Section 4.5 will highlight on the “Adsorption Isotherms”, which involves in this separation process.

4.1 Effects of Initial Dye Concentration in Dye Removal

In this section, the results retrieved from the performed experiments, which investigates the effects of initial dye concentration in dye removal are being presented and discussed at the same time. The effects of initial dye concentration on dye removal can be carried out by preparing the absorbent-absorbate (ionic liquid-dye) solution with constantly fixed amount of [BMIM]- hexafluorophosphate (ionic liquid) at 1 gram as well as fixed volume of dye wastewater at 10 milliliters for each test. Manipulation is done on the concentration of dye content in wastewater ranging from 250ppm-500ppm with 50ppm increment for each test interval. The following are the data obtained from this experiment, which are tabulated into tables and plotted into graphs.

Table 4.1.1: Effect of Dye Removal at 500ppm of Dye in Wastewater

Time Interval (hours)	Absorbance	Concentration (ppm)
0	0	500.00
1.5	0.302	147.67
3	0.095	78.67
4.5	-0.017	41.33
6	-0.03	37.00
7.5	-0.03	37.00

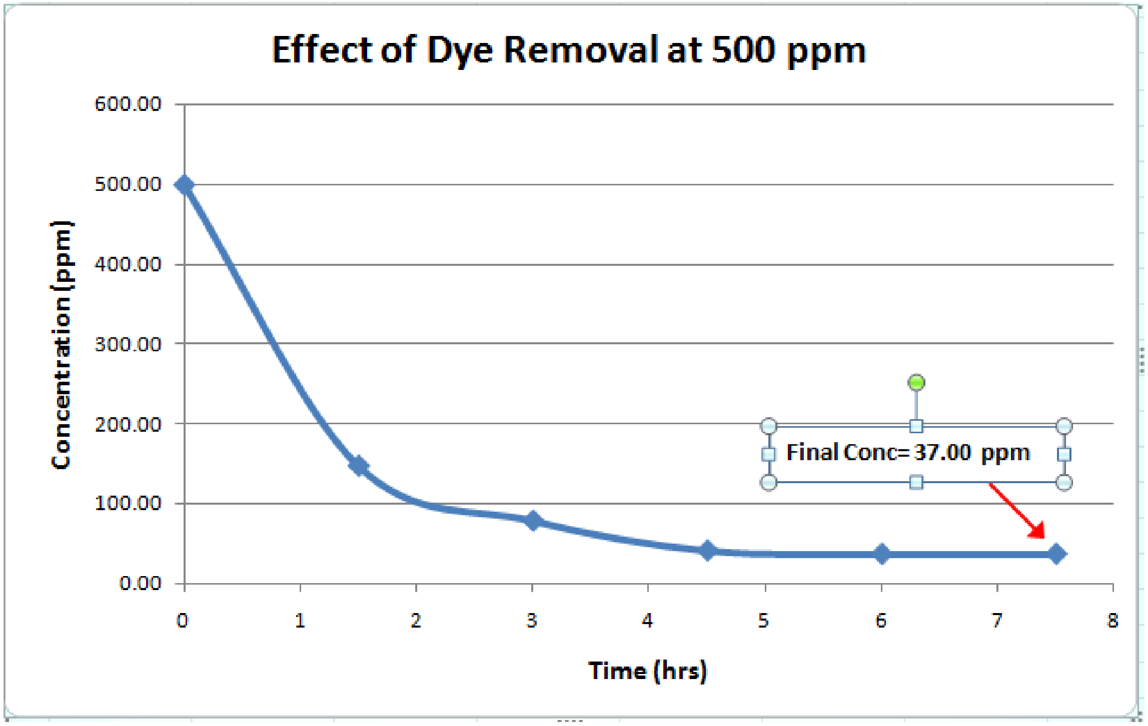


Figure 4.1.1: Effect of Dye Removal at 500ppm of Dye in Wastewater

Table 4.1.1 shows the data tabulated from the experiments of investigating the effect of dye removal at 500ppm of dye in wastewater. For every 1.5 hours interval, a sample of wastewater was obtained and the sampling continued until 5 samples were obtained. The collected samples were then taken for analysis by utilizing the UV-Vis spectrophotometer. The absorbance values obtained from the analysis results were then compared to the standard calibration curve in order to determine the concentration of dye in the wastewater after a specific duration of separation process. After the concentrations of dye for each time interval had been determined, the values are then tabulated into table and plotted into a graph. Based on Figure 4.1, the concentration detected decreases with time as the duration of agitation furthers and eventually remains constant at 37ppm without further reduction after 4.5 hours of agitation. This can be explained where the active sites on the absorbent surface, which is the [BMIM] hexafluorophoshate had been fully occupied by the Phenol Red dye. This leaves no more actives sites on the absorbent to bind the remaining Phenol Red dye available in the wastewater.

Similar phenomena can also be seen in all samples tested at varied concentration of dye content in wastewater. The following figures show the graphs of concentration versus time interval for 450ppm, 400ppm, 350ppm, 300ppm and 250ppm, respectively.

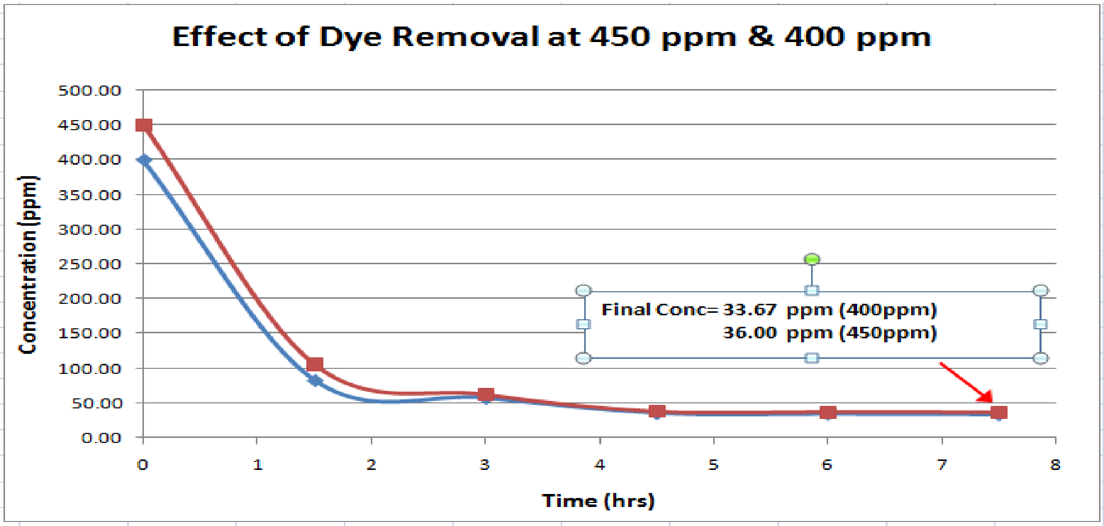


Figure 4.1.2: Effect of Dye Removal at 450ppm (Red) & 400ppm (Blue) of Dye in Wastewater

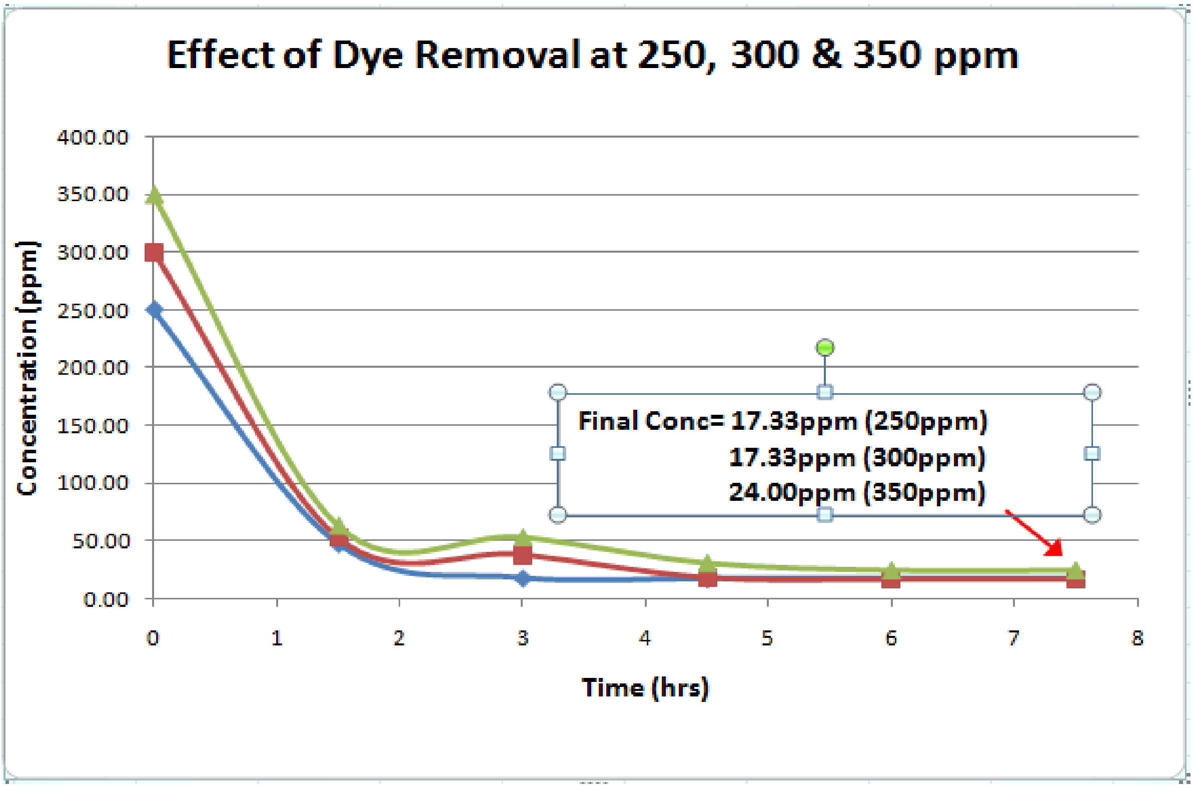


Figure 4.1.3: Effect of Dye Removal at 350ppm (Green), 300ppm (Red) 250ppm (Blue) of Dye in Wastewater

As observed in the above graphs of concentration vs time interval, the final concentration after 7.5 hours of agitation reduces when lower initial dye concentration of wastewater was tested. This further confirms that when the concentration of dye content in wastewater affects the amount of dye being removed. Increasing the amount of dye particles will cause the required active sites on ionic liquid for adsorption of dye molecules to increase. Since the amount of ionic liquid used for all the tests is equal, there will be insufficient adsorption sites to bind the remaining dye molecule available in the wastewater. The ionic liquid is said to be the limiting agent for the separation process. Figure 4.1.5 & Table 4.1.2 show the dye removal efficiency at varied initial dye concentration.

Table 4.1.2 : Dye Removal Efficiency at Varied Concentration of Dye in Ionic Liquid

Concentration (ppm)	**Dye Removal Efficiency (%)**
250	85.60
300	82.22
350	82.00
400	79.25
450	76.67
500	70.47

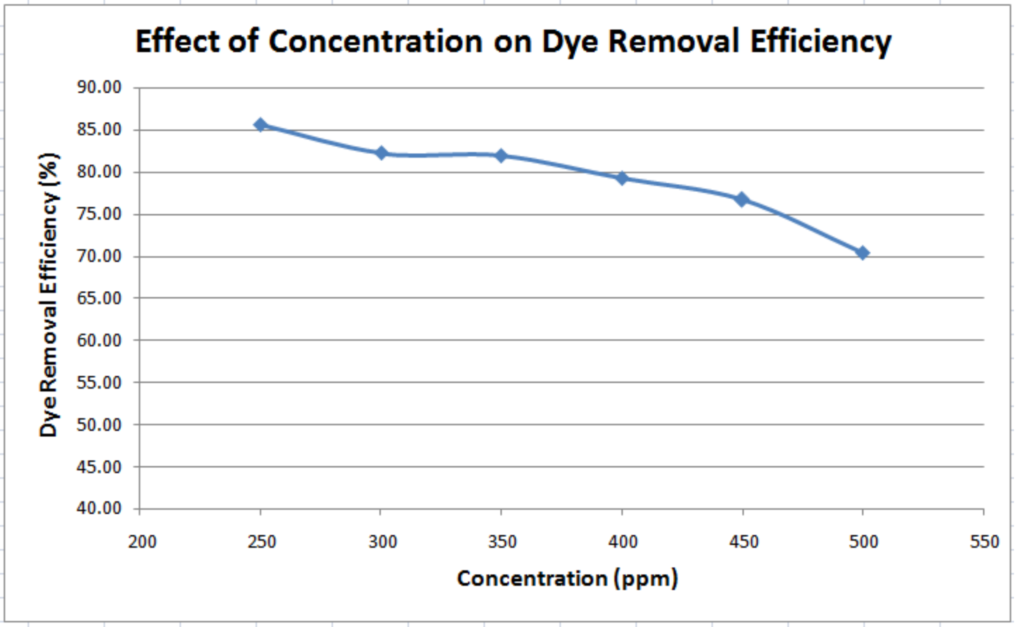


Figure 4.1.4: Effect of Concentration on Dye Removal Efficiency at t = 7.5 hours

The percentage of dye removal efficiency is calculated based on the following equation (Absalan et. al., 2011):

$$Dye\ Removal\ Efficiency = \frac{C_o - C_f}{C_o} \text{ x } 100\%$$

Where, C_o *= Initial dye concentration in wastewater*

C_f *= Final dye concentration after separation*

As the final concentration at 7.5 hours does not provide distinct differences among all the 6 test results. Therefore, the concentration at 1.5 hours is taken as the final concentration for each sample. Below is the sample calculation of dye removal efficiency for the effect of dye removal at 500ppm.

$C_o = 500ppm$

$C_f = 147.67ppm$

$$Dye\ Removal\ Efficiency = \frac{500 - 147.67}{500} \text{ x } 100\%$$

$$= 70.47\%$$

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial of dye concentration factor depends on the immediate relation between

the concentration of the dye and the available binding sites on an adsorbent surface, which is the ionic liquid. As observed in Figure 4.5, the percentage of dye removal decreases with an increase in the initial dye concentration, which is due to the saturation of adsorption sites with the dye molecules on the adsorbent surface according to Amran et. al, (2011). At a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will be insufficient for the remaining dye molecules. On the other hand, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this is subject to the high driving force for mass transfer at a high initial dye concentration according to Garg et. al, (2004).

4.2 Effects of Temperature in Dye Removal

For this section, the results retrieved from the performed experiments, which investigates the effects of temperature in dye removal are being presented and discussed after that. The effects of temperature in dye removal can be carried out by preparing the absorbent-absorbate (ionic liquid-dye) solution with constantly fixed amount of [BMIM]-hexafluorophosphate (ionic liquid) at 1 gram as well as fixed volume and concentration of dye wastewater at 10 milliliters and 250ppm of dye respectively for each test. Manipulation is done on the temperature of wastewater varied in the range between 25^oC-50^oC with 5^oC increment for each test interval. The following are the data obtained from this experiment, which are tabulated into tables and plotted into graphs.

Table 4.2.1: Effect of Dye Removal at 25^oC of Dye in Wastewater

Time Interval (hours)	Absorbance	Concentration (ppm)
0	0	250.00
1.5	0.029	56.67
3	0.011	50.67
4.5	-0.02	40.33
6	-0.045	32.00
7.5	-0.045	32.00

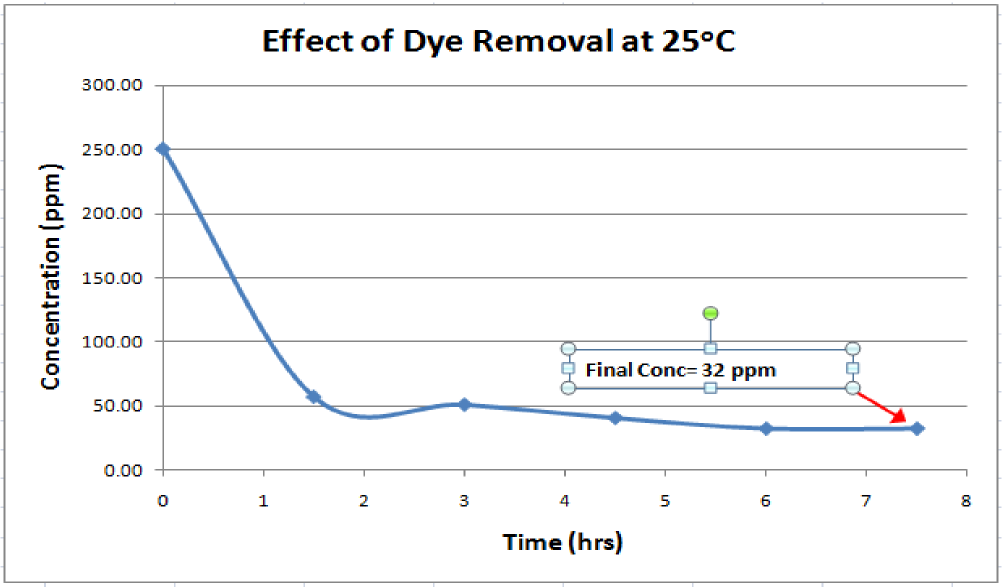


Figure 4.2.1: Effect of Dye Removal at 25°C

Table 4.2.1 shows the data tabulated from the experiments of investigating the effects of dye removal at 25°C of dye in wastewater. For every 1.5 hours interval, a sample of wastewater was obtained and the sampling continued until 5 samples were obtained. The collected samples were then taken for analysis by utilizing the UV-Vis spectrophotometer. The absorbance values obtained from the analysis results were then compared to the standard calibration curve in order to determine the concentration of dye in the wastewater after a specific duration of separation process. After the concentrations of dye for each time interval had been determined, the values are then tabulated into table and plotted into a graph. Based on Figure 4.2.1, the concentration detected decreases with time as the duration of agitation furthers and eventually started to remain constant at 32ppm without further reduction after 6 hours of agitation. This can be explained where the active sites on the absorbent surface, which is the [BMIM] hexafluorophoshate had been fully occupied by the Phenol Red dye. This leaves no more actives sites on the absorbent to bind the remaining Phenol Red dye available in the wastewater.

Similar phenomena can also be seen in all samples tested at varied temperature of dyed wastewater. The following figures show the graphs of concentration versus time interval for 30°C, 35°C, 40°C, 45°C, 50°C, respectively.

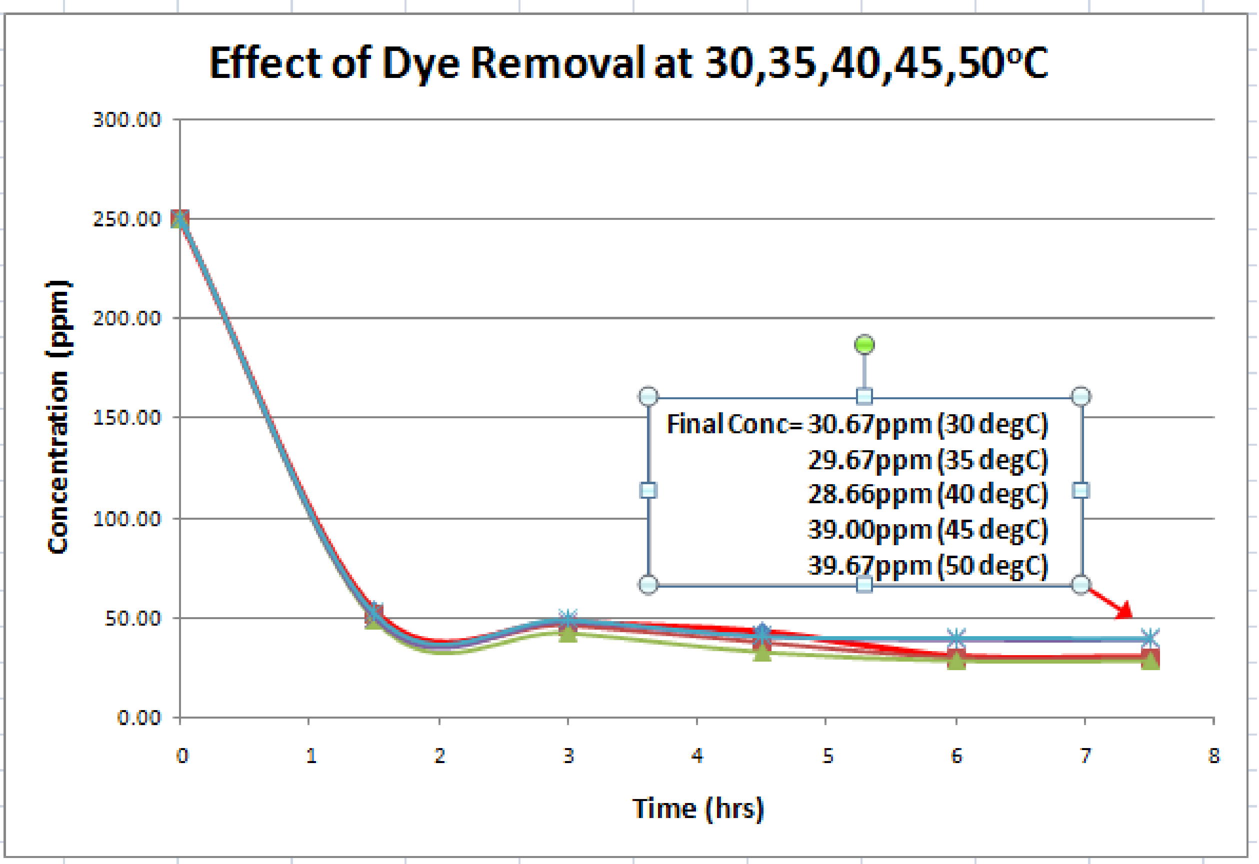


Figure 4.2.2: Effect of Dye Removal at 30°C (Red), 35°C (Purple), 40°C (Green), 45°C (Pink) & 50°C(Blue)

As observed in the above graphs of concentration vs time interval, the final concentration after 7.5 hours of agitation reduces when increasing the temperature of wastewater. However, when the wastewater was tested at 45°C and above, there is a sudden increase in the final dye concentration. According to Absalan et.al,(2011), such results indicates that the adsorption process of dye on the ionic liquid is endothermic in nature, which means energy is required during the adsorption process in order to provide the kinetic energy for the dye molecules to move and thus increases the frequency of contact between the ionic liquid and the dye molecules to perform effective adsorption. However, when the temperature increases beyond 45°C, the concentration after 7.5 hours of agitation increases. This is further explained by Absalan et.al, (2011) as well as supported by Al-Degs et. al, (2007) where by the heat energy provided will cause the bond strength between the molecules and the ionic liquid to be weaken, which prevents effective adsorption to occur. Similar to analogy of activation energy of catalyst, where the catalyst will only be activated at certain temperature and becomes deactivated when the temperature is too high for the reaction to occur. The adsorption of dye on the ionic liquid can be effectively perform only up to an optimum temperature and the adsorption efficiency will eventually reduce when the temperature condition goes beyond the optimum temperature for the adsorption. Figure 4.2.5 & Table 4.2.2 show the dye removal efficiency at varied temperature condition of dyed wastewater.

Table 4.2.2: Removal Efficiency at Varied Temperature of Dyed Wastewater

Temperature (°C)	Dye Removal Efficiency (%)
25	87.20
30	87.73
35	88.13
40	88.53
45	84.40
50	84.13

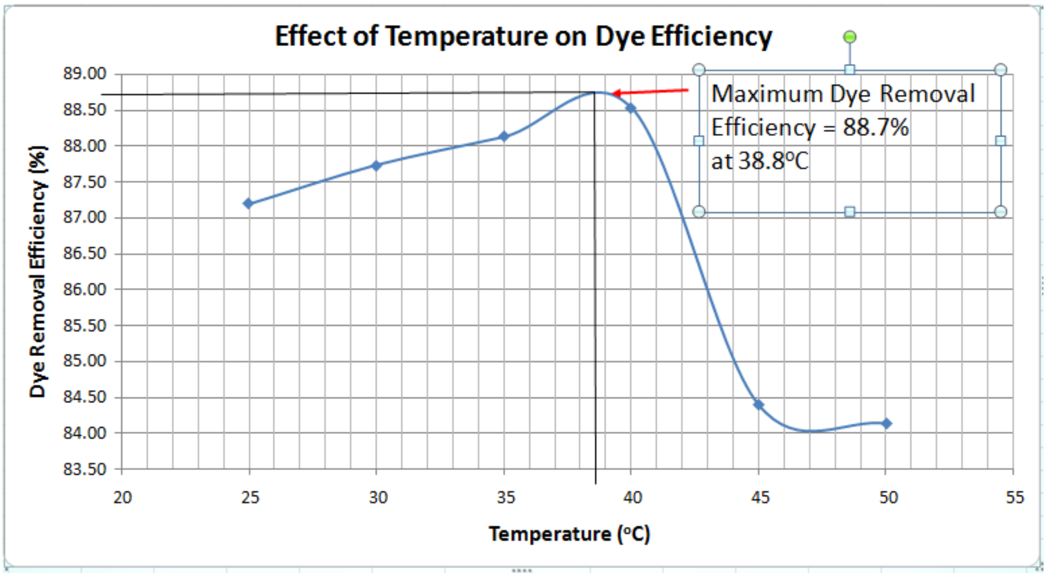


Figure 4.2.3: Effect of Temperature on Dye Removal Efficiency at t = 7.5 hours

The percentage of dye removal efficiency is calculated based on the following equation (Absalan et.al., 2011):

$$\textit{Dye Removal Efficiency} = \frac{C_o - C_f}{C_o} \text{ x } 100\%$$

Where, C_o = *Initial dye concentration in wastewater*

C_f = *Final dye concentration after separation*

The concentration at 7.5 hours is taken as the final concentration for each sample. Below is the sample calculation of dye removal efficiency for the effect of dye removal at 25°C.

C_o = *250ppm*

C_f = *32ppm*

$$\textit{Dye Removal Efficiency} = \frac{250 - 32}{250} \text{ x } 100\%$$

$$= 87.2\%$$

By observing the plot of "Effect of Temperature on the Dye Removal Efficiency", the dye removal efficiency increases as the temperature reaches up to 38.8^{o}C. Beyond this temperature, the removal efficiency of the dye by the ionic liquid drastically reduced from 88.7% to 84 percent. As mentioned before, increase in temperature may increase the dye removal efficiency of the ionic liquid but at the same time, when the temperature condition for the separation goes beyond 38.8^{o}C, the bond strength between the ionic liquid and the dye molecules weakens by the heat energy and thus preventing the adsorption process to be carried out efficiently. Further temperature increase of the dyed wastewater is not being analyzed since the water will vapourised at high temperature and thus unable to perform the dye separation from the wastewater.

4.3 Effects of Phase Ratio in Dye Removal

For this section, the results retrieved from the performed experiments, which investigates the effects of phase ratio in dye removal are being presented and discussed after that. The effects of phase ratio in dye removal can be carried out by preparing the absorbent-absorbate (ionic liquid-dye) solution with constantly fixed amount of [BMIM]-hexafluorophosphate (ionic liquid) at 1 ml as well as fixed concentration of dye wastewater at 250ppm of for each test. Manipulation is done on the volume of dyed wastewater varied in the range between 10 ml to 60 ml with 10 ml increment for each test interval. Thus, the ratio of ionic liquid to the dyed wastewater varies as well, where by the tested ratios (Vol ionic liquid : Vol dye wastewater) are 1:10, 1:20, 1:30, 1:40, 1:50 and 1:60. The following are the data obtained from this experiment, which are tabulated into tables and plotted into graphs.

Table 4.3.1: Effect of Dye Removal at Phase Ratio of 1:10

Time Interval (hours)	Absorbance	Concentration (ppm)
0	0	250.00
1.5	0.033	58.00
3	0.014	51.67
4.5	-0.018	41.00
6	-0.038	34.33
7.5	-0.039	34.00

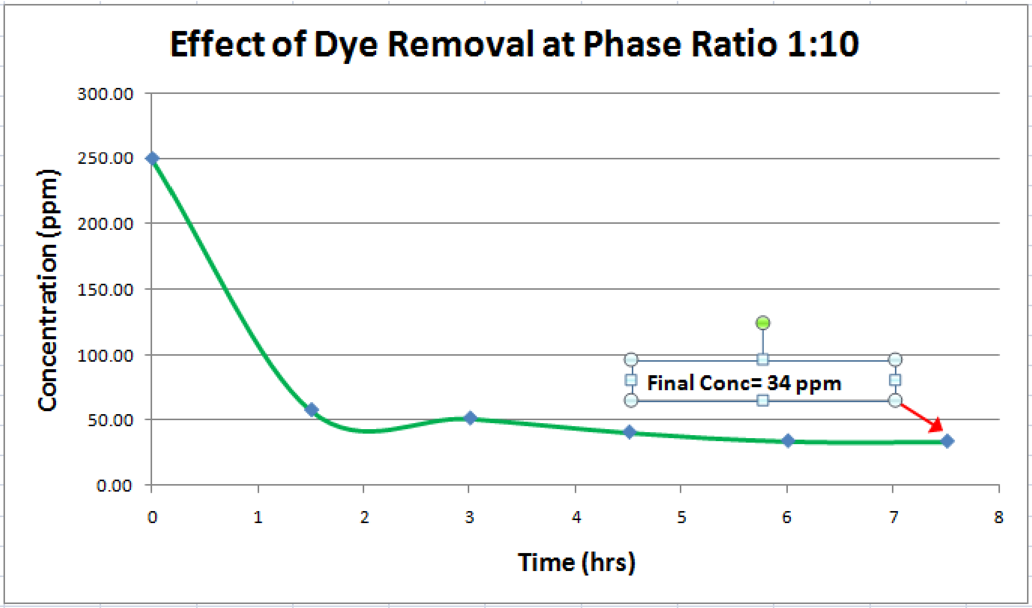


Figure 4.3.1: Effect of Dye Removal at Phase Ratio 1:10

Table 4.3.1 shows the data tabulated from the experiments of investigating the effects of dye removal at phase ratio of 1:10 of ionic liquid and dyed wastewater. For every 1.5 hours interval, a sample of wastewater was obtained and the sampling continued until 5 samples were obtained. The collected samples were then taken for analysis by utilizing the UV-Vis spectrophotometer. The absorbance values obtained from the analysis results were then compared to the standard calibration curve in order to determine the concentration of dye in the wastewater after a specific duration of separation process. After the concentrations of dye for each time interval had been determined, the values are then tabulated into table and plotted into a graph. Based on Figure 4.3.1, the concentration detected decreases with time as the duration of agitation furthers and eventually started to remain constant at 34ppm without further reduction after 6 hours of agitation. This can be explained where the active sites on the absorbent surface, which is the [BMIM] hexafluorophoshate had been fully occupied by the Phenol Red dye. This leaves no more actives sites on the absorbent to bind the remaining Phenol Red dye available in the wastewater. Similar phenomena can also be seen in all samples tested at varied temperature of dyed wastewater. The following figures show the graphs of concentration versus time interval for phase ratio of 1:20, 1:30, 1:40, 1:50 and 1:60 respectively.

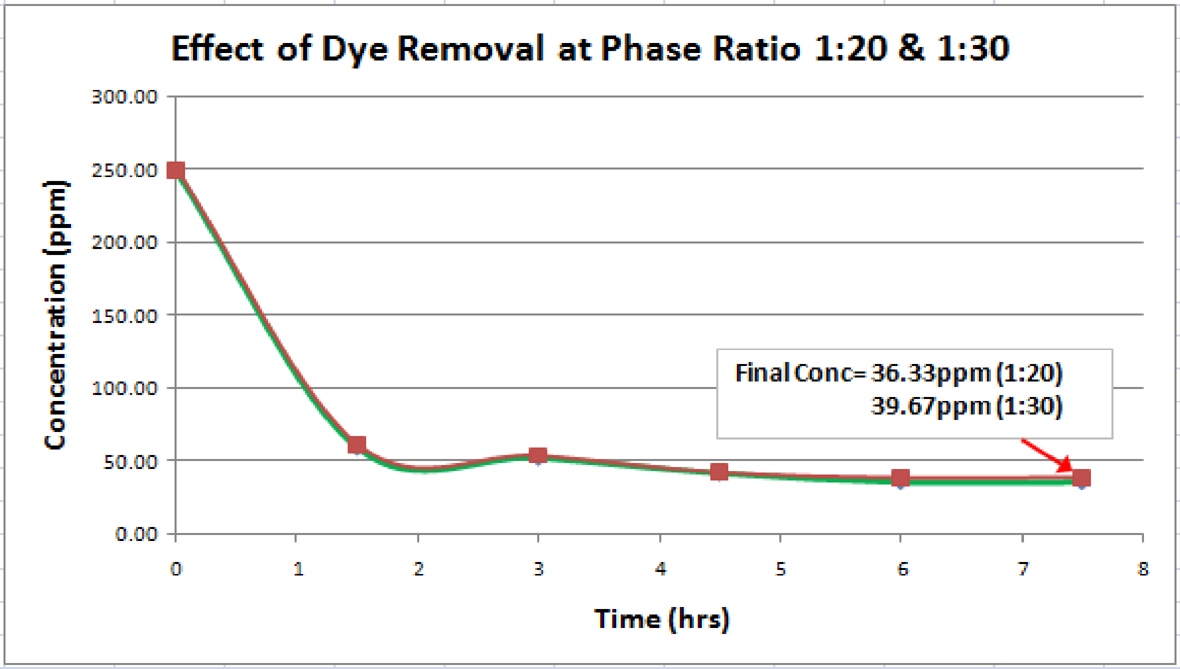


Figure 4.3.2: Effect of Dye Removal at Phase Ratio 1:20 (Green) and 1:30 (Red)

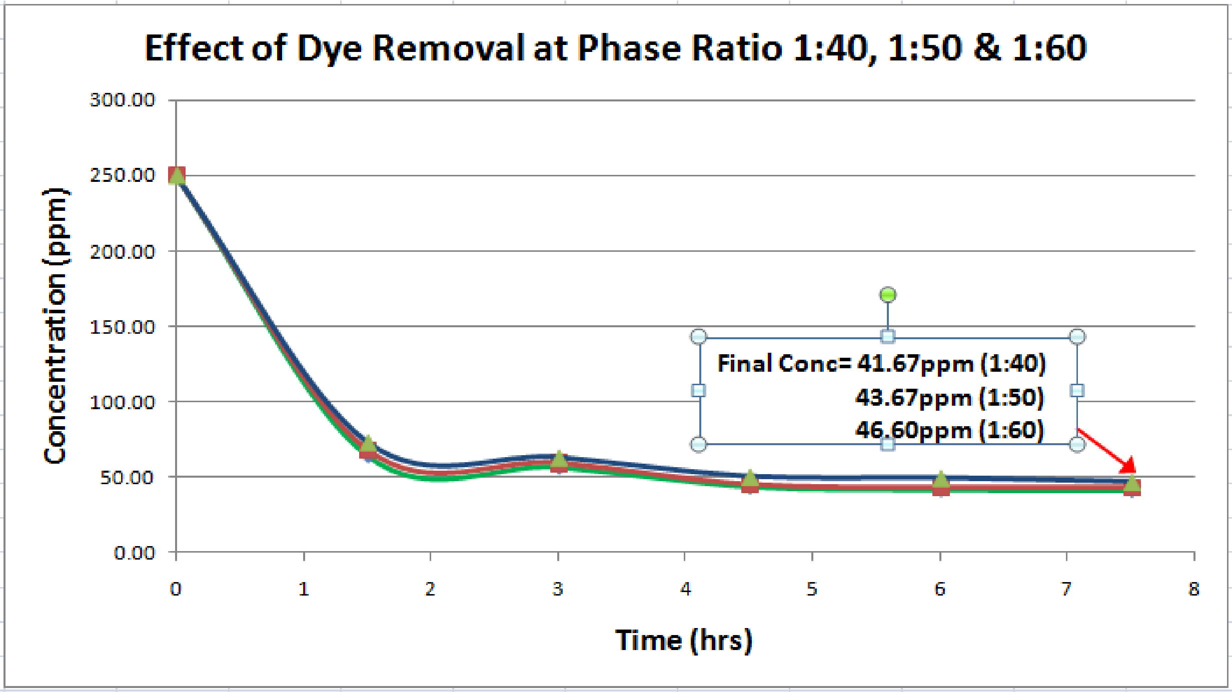


Figure 4.3.3: Effect of Dye Removal at Phase Ratio 1:40 (Red), 1:50 (Green), 1:60 (Blue)

As observed in the above graphs of concentration vs time interval, the final concentration after 7.5 hours of agitation reduces when increasing the volume of dyed wastewater per volume of ionic liquid. The justification of this phenomenon is somehow similar to the effects of initial dye concentration in dye removal, where the insufficient amount of ionic liquid to provide active sites for the adsorption of the remaining excess dye molecules as the volume of wastewater increases. Another reason for the reduction in the adsorption efficiency with the increment of phase ratio is due to the larger volume of wastewater than the ionic liquid, which causes some of the dye molecules to not fully come in to contact with the ionic liquid. Since the agitation time for each test was equal, which was set for a duration of 7.5 hours, the frequency of contact between the dye and the ionic liquid will be lesser for the larger phase ratio test. Apart from that, the higher density of ionic liquid than the dye wastewater further reduces the frequency of contact since most of the time, the ionic liquid settles at the bottom of the solution without contacting the upper surface of the dye solution during agitation. The adsorption rate will be less when the frequency of contact between the ionic liquid and dye reduces, which can be clearly seen at larger phase ratio. Figure 4.3.5 & Table 4.3.2 show the dye removal efficiency at varied phase ratio of ionic liquid to dyed wastewater.

Table 4.3.2: Effect of Phase Ratio in Dye Removal Efficiency

Phase Ratio (Vol Ionic Liquid/Vol Dyed Wastewater)	Dye Removal Efficiency
0.1	86.40
0.05	85.47
0.0333	84.13
0.025	83.33
0.02	82.53
0.0167	81.33

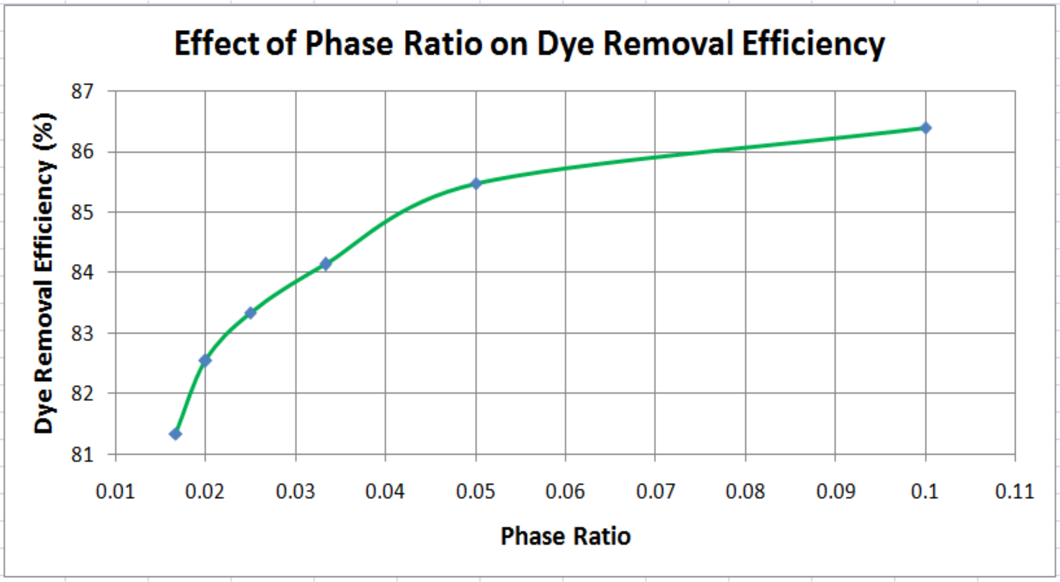


Figure 4.3.4: Effect Phase Ratio on Dye Removal Efficiency at t = 7.5 hours

The calculation of the dye removal efficiency for each phase ratio is similar to the previous parameters investigated, where by the final concentration after 7.5 hours of agitation is taken. By observing the plot above, the dye removal efficiency is higher as the volume of ionic liquid per volume of dye wastewater increases. A drastic reduction in dye removal efficiency can be seen when lower phase ratio condition is applied. Therefore, it can be justified that at constant volume of ionic liquid, lower volume of dyed wastewater is preferred in order to perform an effective adsorption process.

4.4 Effects of pH of Dyed Wastewater in Dye Removal

For this section, the results retrieved from the performed experiments, which investigates the effects of pH of dyed wastewater in dye removal are being presented and discussed later. The effects of phase ratio in dye removal can be carried out by preparing the absorbent-absorbate (ionic liquid-dye) solution with constantly fixed amount of [BMIM]-hexafluorophosphate (ionic liquid) at 1g as well as fixed concentration and volume of dye wastewater at 250ppm and 10ml, respectively for each test. Manipulation is done on the pH of dyed wastewater varied in the range between 3.8 to 8.6 ml with approximately increment of pH 1.2 for each test interval. The following are the data obtained from this experiment, which are tabulated into tables and plotted into graphs.

Table 4.4.1: Effect of pH in Dye Removal

Time Interval (hours)	Absorbance	Concentration (ppm)
0	0	250.00
1.5	0.078	73.00
3	0.048	63.00
4.5	0.01	50.33
6	0.007	49.33
7.5	-0.001	46.67

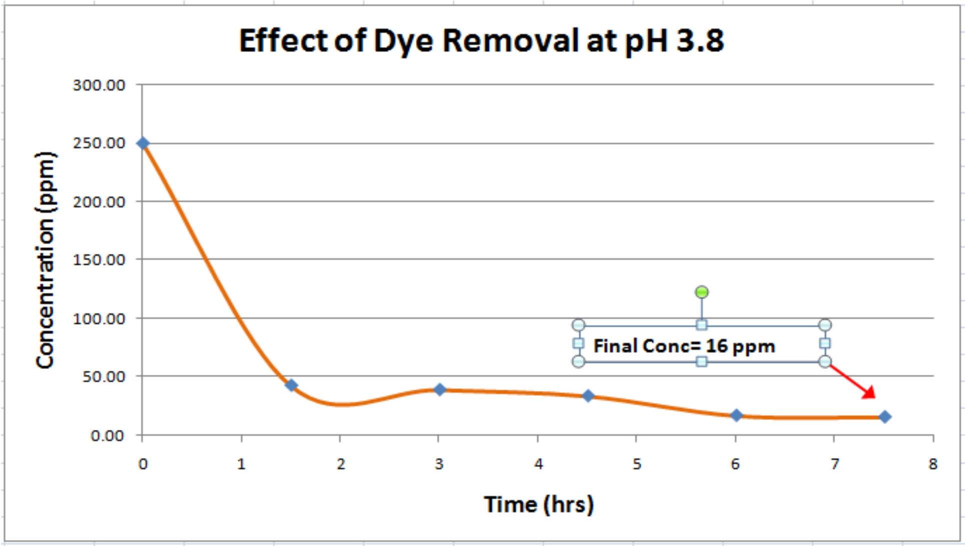


Figure 4.4.1: Effect of pH in Dye Removal Efficiency at t = 7.5 hours

Table 4.4.1 shows the data tabulated from the experiments of investigating the effects of dye removal at pH 3.8 of dye in wastewater. For every 1.5 hours interval, a sample of wastewater was obtained and the sampling continued until 5 samples were obtained. The collected samples were then taken for analysis by utilizing the UV-Vis spectrophotometer. The absorbance values obtained from the analysis results were then compared to the standard calibration curve in order to determine the concentration of dye in the wastewater after a specific duration of separation process. After the concentrations of dye for each time interval had been determined, the values are then tabulated into table and plotted into a graph. Based on Figure 4.4.1, the concentration detected decreases with time as the duration of agitation furthers and eventually started to remain constant at 16ppm without further reduction after 6 hours of agitation. This can be explained where the active sites on the absorbent surface, which is the [BMIM] hexafluorophoshate had been fully occupied by the Phenol Red dye. This leaves no more actives sites on the absorbent to bind the remaining Phenol Red dye available in the wastewater.

Similar phenomena can also be seen in all samples tested at varied temperature of dyed wastewater. The following figures show the graphs of concentration versus time interval for pH values of 4.4, 5.5, 6.3, 7.7 and 8.6 respectively.

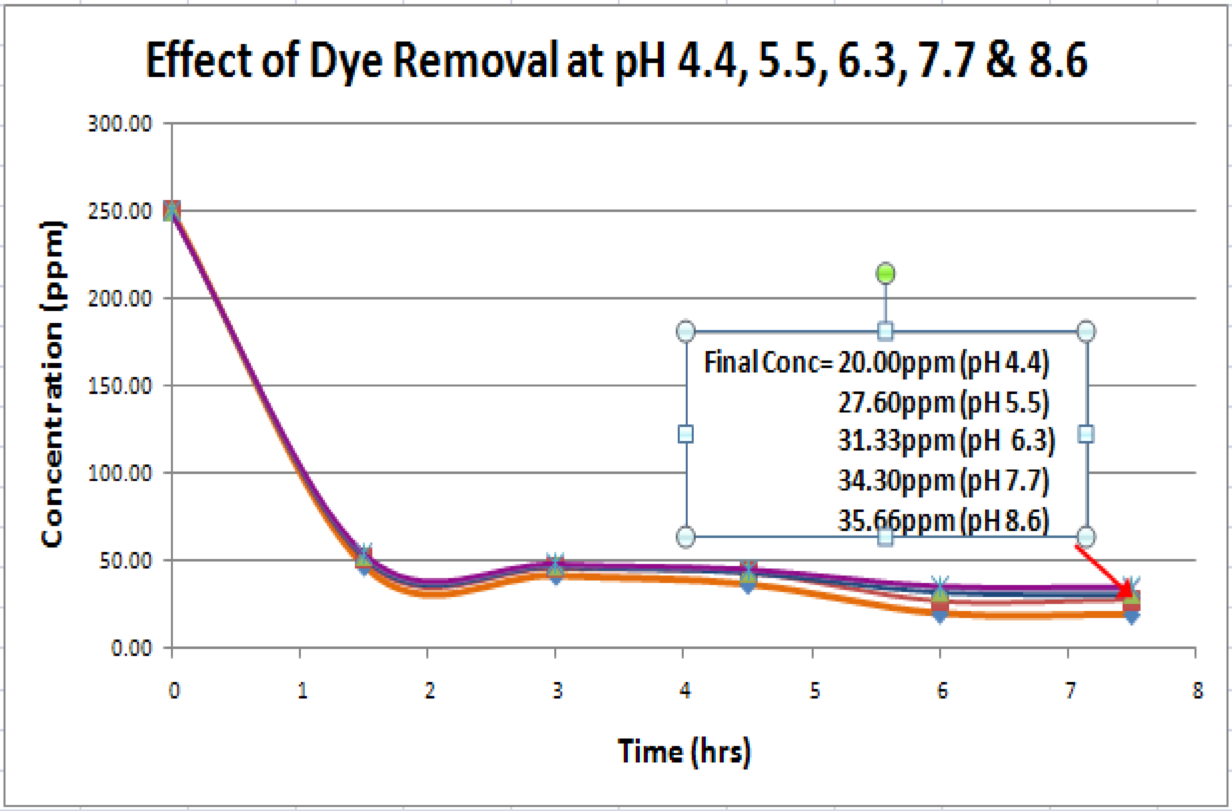


Figure 4.4.2: Effect of Dye Removal at pH 4.4 (blue), 5.5 (Orange), 6.3(Pink), 7.7(green), 8.6(Purple)

As observed in the above graphs of concentration vs time interval, the final concentration after 7.5 hours of agitation reduces when increasing the pH of wastewater. According to Kamboh et. al (2011), the changes of pH of dyed wastewater affects the adsorptive process through dissociation of functional groups on the active sites of the sorbent. Phenol Red dye is comparatively a large molecule and contains hydroxyl groups and upon dissolution in aqueous media, these groups can easily dissociate and thus, the dye molecule becomes negatively charged at higher pH. Since [BMIM] hexafluorophosphate is an cationic type of ionic liquid that contains positive charged ions, the lower sorption above the pH 7 contributes to the abundance of OH^- ions, which creates a competing environment with the anionic Phenol Red dye in binding with the active sites at the surface of the positively charged ionic liquid. Figure 4.4.5 & Table 4.4.2 show the dye removal efficiency at varied temperature condition of dyed wastewater.

Table 4.4.2: Effect of Phase Ratio in Dye Removal Efficiency

pH	Dye Removal Efficiency (%)
3.8	93.60
4.4	92.00
5.5	88.93
6.3	87.47
7.7	86.27
8.6	85.73

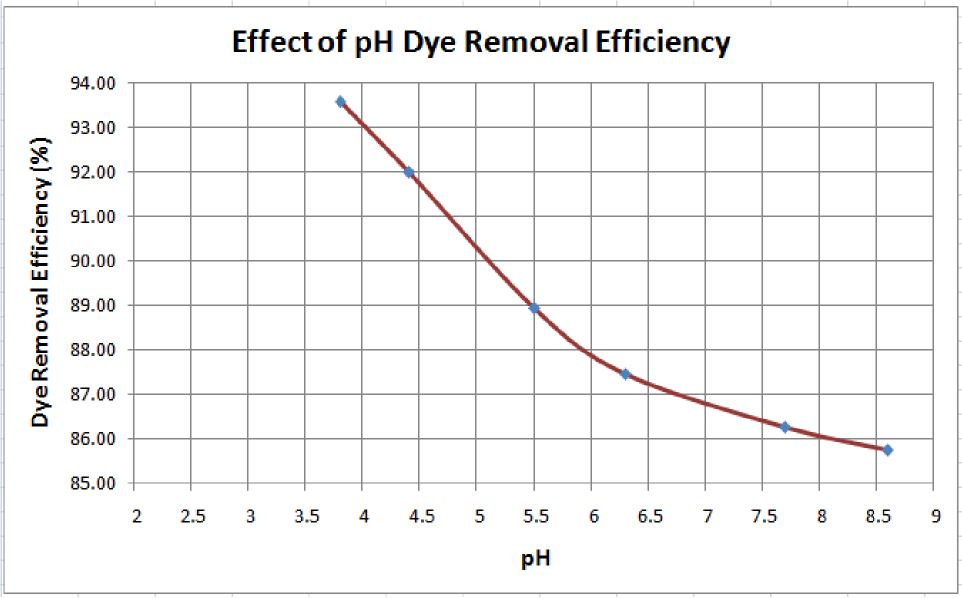


Figure 4.4.3: Effect of pH in Dye Removal Efficiency at t =7.5 hours

The calculation of the dye removal efficiency for each phase ratio is similar to the previous parameters investigated, where by the final concentration after 7.5 hours of agitation is taken. By observing the plot above, the dye removal efficiency is higher at low pH region of dye wastewater, which is able to reach 93.6% of adsorption efficiency. A drastic reduction in dye removal efficiency can be seen when higher pH condition is applied. Another observation can be done is that the effects of pH is more significant than the effects of temperature towards the dye removal efficiency, where by the changes in efficiency reduces approximately 2% for every pH 1.2 increase. According to Salleh M.A.M et. al (2011), pH is a very important factor in the adsorption process. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result the rate of adsorption will vary with the pH of an aqueous medium. At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged. As a result, anionic dye of Phenol Red shows a decrease in adsorption rate. In contrast, at a low pH solution, the positive charge on the solution interface will increase and the adsorbent surface appears positive charged, which results in an increase in anionic dye adsorption. Therefore, it can be justified that at constant volume of ionic liquid, lower pH of dyed wastewater is preferred in order to perform an effective adsorption process.

4.5 Dye Removal at Optimum Condition & Isotherms Involved

For this section, the results retrieved from the performed experiments, which investigates the effects towards the dye removal efficiency when the adsorption condition is at optimum condition are being presented and discussed later. This can be carried out by preparing the absorbent-absorbate (ionic liquid-dye) solution with constantly fixed amount of [BMIM]-hexafluorophosphate (ionic liquid) at 1g as well as fixed concentration and volume of dye wastewater at 250ppm and 10ml, respectively for each test. Manipulation is done on the pH of dyed wastewater, which is set at optimum condition at pH 3.8 and at an optimum temperature of 38°C The following are the data obtained from this experiment, which are tabulated into tables and plotted into graphs.

Table 4.5.1: Effect of Dye Removal at Optimum Condition

Time Interval (hours)	Absorbance	Concentration (ppm)
0	0	250.00
1.5	-0.012	32.00
3	-0.023	28.70
4.5	-0.039	24.00
6	-0.089	11.13
7.5	-0.093	10.56

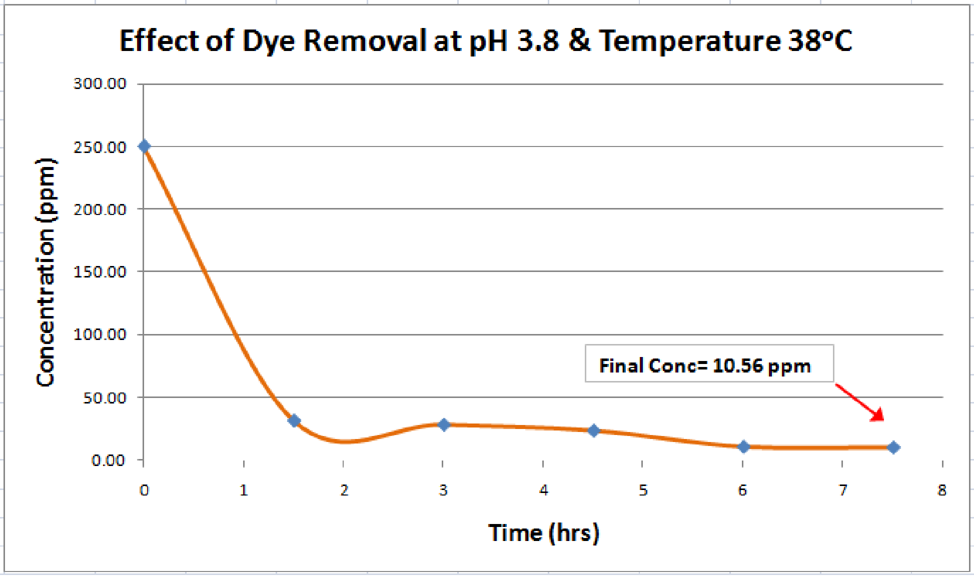


Figure 4.5.1: Effect of Dye Removal at Optimum Condition

Table 4.5.1 shows the data tabulated from the experiments of investigating the effects of dye removal at optimum temperature and pH of the dyed wastewater. For every 1.5 hours interval, a sample of wastewater was obtained and the sampling continued until 5 samples were obtained. The collected samples were then taken for analysis by utilizing the UV-Vis spectrophotometer. The absorbance values obtained from the analysis results were then compared to the standard calibration curve in order to determine the concentration of dye in the wastewater after a specific duration of separation process. After the concentrations of dye for each time interval had been determined, the values are then tabulated into table and plotted into a graph. Based on Figure 4.5.1, the concentration detected decreases with time as the duration of agitation furthers and eventually started to remain constant at 10.56ppm without further reduction after 6 hours of agitation. This can be explained where the active sites on the absorbent surface, which is the [BMIM] hexafluorophoshate had been fully occupied by the Phenol Red dye. This leaves no more actives sites on the absorbent to bind the remaining Phenol Red dye available in the wastewater. The final concentration of dye in wastewater obtained after 7.5 hours of agitiation is by far the lowest among the previous experimental results with the reading of 10.56ppm. Following is the calculation of dye removal efficiency at optimum condition (Absalan et.al.,2011).

$$Dye\ Removal\ Efficiency = \frac{C_o - C_f}{C_o} \text{ x } 100\%$$

Where, C_o = Initial dye concentration in wastewater

C_f = Final dye concentration after separation

The concentration at 7.5 hours is taken as the final concentration for this experiement. Below is the sample calculation of dye removal efficiency for the effect of dye removal at optimum condition.

$C_o = 250ppm$

$C_f = 10.56ppm$

$$Dye\ Removal\ Efficiency = \frac{250 - 10.56}{250} \text{ x } 100\%$$

$$= 95.77\%$$

At optimum condition, the low pH condition of the adsorption process provides the positive charged environment with the presence of H^+ ions on the solution interface will increase and the adsorbent surface appears positive charged, which results in an increase in anionic dye adsorption. In addition to that, the adsorption process of dye on the ionic liquid is endothermic in nature, which means energy is required during the adsorption process in order to provide the kinetic energy for the dye molecules to move and thus increases the frequency of contact between the ionic liquid and the dye molecules to perform effective adsorption. Only at optimum condition can the highest separation be achieved by this adsorption process, which is at 95.77%.

Following is the calculation of isotherms, table and plot for the calculated isotherms

$$\textit{Adsorption Capacity, } Q_e = \frac{V(C_o - C_f)}{M}$$

Where, C_o *= Initial dye concentration in wastewater*
C_f *= Final dye concentration after for every interval*
V *=Volume of Dye Wastewater*
M *=Mass of ionic liquid*

The concentration at 1.5 hours intervals are taken as the final concentration for this experiment. Below is the sample calculation of dye removal efficiency for the effect of dye removal at optimum condition.

C_o *= 250ppm*
C_f *= 32ppm*
V *=10ml / 0.010 l*
M *= 1 g*

$$\textit{Adsorption Capacity, } Q_e = \frac{0.01(250 - 32)}{1}$$

$$= 3.847 \text{ mg dye/ g}$$

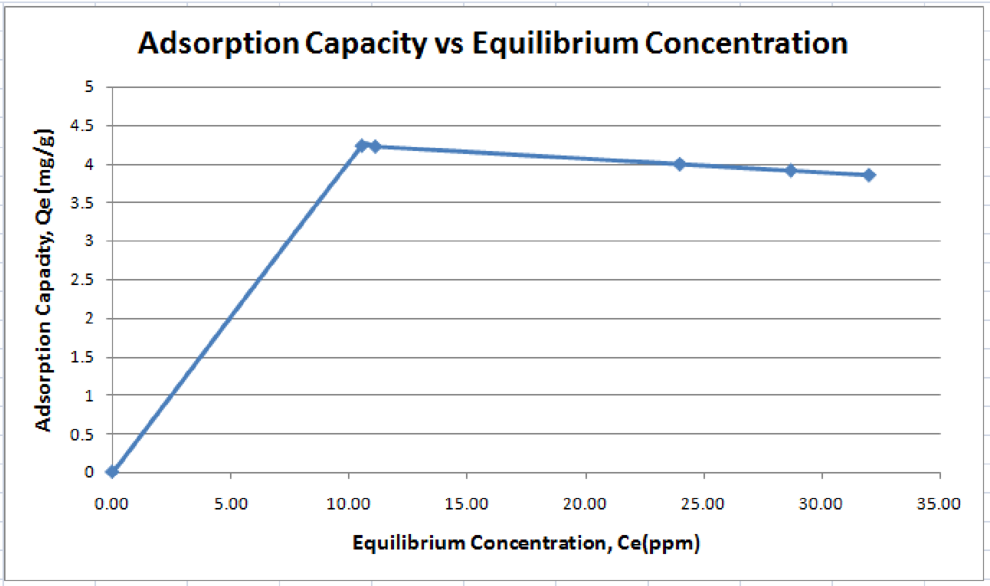


Figure 4.5.2: Adsorption Capacity at Optimum Condition.

As observed in Figure 4.5.2, the adsorption capacity decreases as the equilibrium concentration increases. This means that as the concentration decreases along the 7.5 hours of agitation, the adsorption process of dye on the ionic liquid is still ongoing without any increment in the dye concentration in water. This indicates that the dye molecules binded on the active sites of the ionic liquids does not experience any weaken in their bonding that releases the dye molecules from the ionic liquid if it occurred. Since this regular isotherm is not able to display types of adsorption undergo in this separation process whether it is a monolayer or multilayer dye adsorption, two isotherms were introduced, namely Langmuir's and Freundlich's Isotherms. Adsorption that favors the Langmuir's isotherm are said to be a monolayer adsorption where the dye molecules will be adsorbed on the surface of the ionic liquid as a single layer surface. If the adsorption favors the Freundlich's isotherm, the adsorption is said to be a multilayer one as the dye molecules will form another adsorption layer on top of the already occupied active sites of the ionic liquids. The following are the calculations, tables as well as the plots of the two isotherms to determine the type of adsorption for this dye removal process.

The Linearized Langmuir's Isotherm Equation (Absalan et.al.,2011) *are:*

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$$

Where, C_e *= Equilibrium Concentration mg/l*

q_e *= Adsorption Capacity at Equilibrium Concentration, mg dye / g IL*

q_{max} *= Maximum Adsorption Capacity, mg dye / g IL*

b *= Coefficient of Adsorption Energy*

Table 4.5.2: Langmuir Isotherm

Conc at Equilibrium, Ce (ppm)	**Ce/Qe (g/L)**
32.00	8.318042813
28.70	7.348998343
24.00	6.017699115
11.13	2.640348307
10.56	2.499164718
0.00	0

The concentration at equilibrium will be plotted in the x-axis while the Ce/Qe will be plotted to the y-axis and $1/q_{max}$ will be the gradient adhering to the linearized equation.

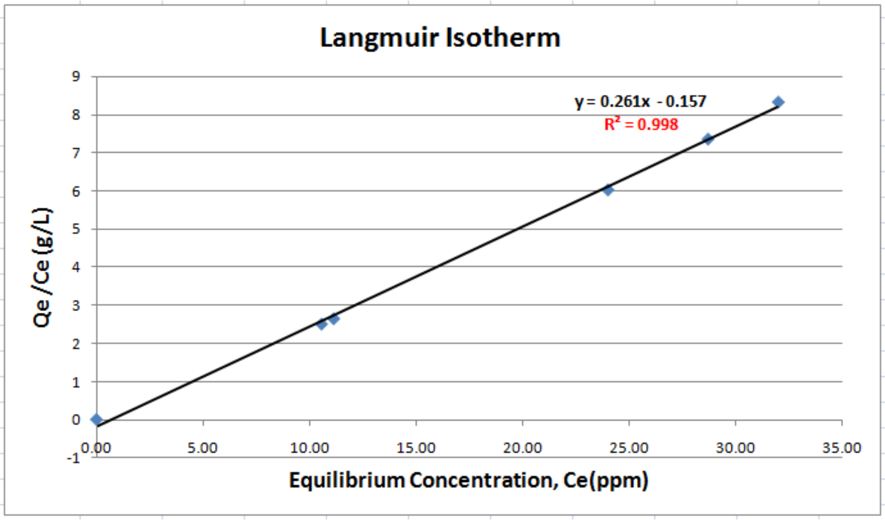


Figure 4.5.3: Linear Plot of the Langmuir Isotherm.

The Linearized Freundlich's Isotherm Equation (Absalan et.al.,2011) *are:*

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where, C_e = *Equilibrium Concentration mg/l*

q_e = *Adsorption Capacity at Equilibrium Concentration, mg dye / g IL*

n = *Coefficient of strength of adsorption*

K_f = *Capacity of absorbent on absorbate*

The log concentration, log C_e at equilibrium will be plotted in the x-axis while the log adsorption capacity, log Qe will be plotted to the y-axis and 1/n will be the gradient adhering to the linearized equation.

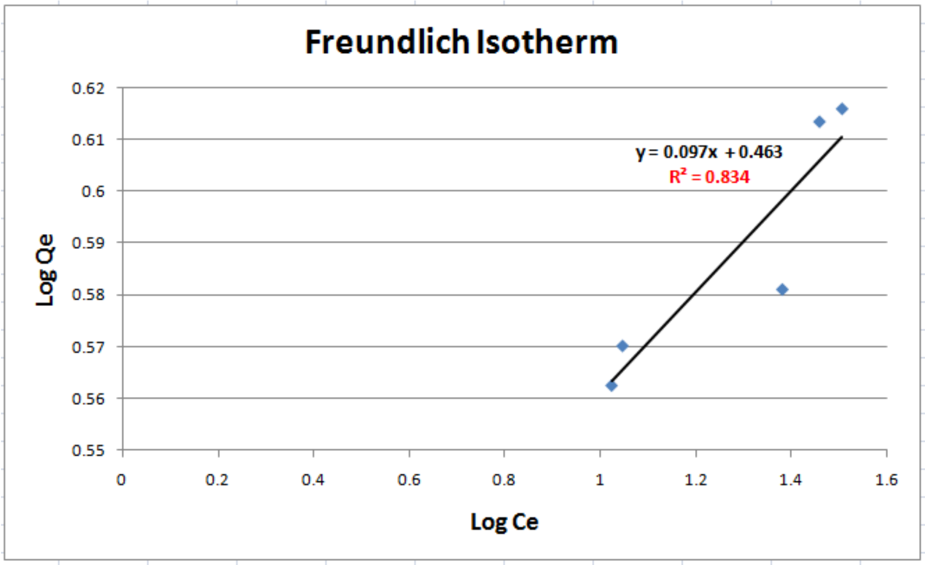


Figure 4.5.4: Linear Plot of the Freundlich's Isotherm.

Based on the observation of both Figure 4.5.3 & Figure 4.5.4, the linear regression, R^2 for the Langmuir plot shows 99.8% while the Freundlich's plot shows 83.4%. This shows that the adsorption process for dye removal strongly favours the Langmuir's Isotherm than that of the Freundlich's Isotherm. According to Absalan.G et. al (2011), adsorption process adhering to the Langmuir's Isotherm occurs as a monolayer adsorption on a homogeneous adsorbent surface. This indicates that the adsorption of dye on the ionic liquid appears to be on a monalayer characteristics on the active sites of the ionic liquid surface with no multilayer formation. The figures below show the dyed wastewater before and after the separation process.

Table 4.5.3:Freundlic***h*** Isotherm

Log Ce	Log Qe
1.505149978	0.615888191
1.457881897	0.613406501
1.380211242	0.581126084
1.046495164	0.570268157
1.023663918	0.562642679

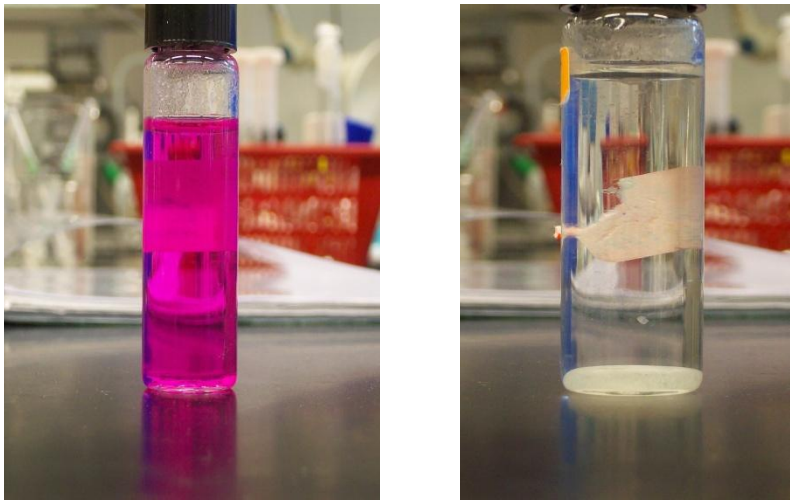


Figure 4.5.5: Condition of Dyed Wastewater Before (Left) and After (Right) Separation.

According to Absalan et.al. (2011) and Robinson, T et.al. (2001), the separation of the phenol red dye from the waste water via ionic liquid is consider as a physical separation rather than a chemical separation. This can be further confirm as the separation appears to be adhering to the Langmuir's Isotherm, where the theory involving such isotherm is a physical separation via adsorption. In addition to that, both the adsorbent (ionic liquid) and treated waste water does not mix miscibly with one another but rather forming 2 phase immiscible fluid before and after the separation.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5 CONCLUSION & RECOMMENDATION

5.1 Conclusion

Based on the above mentioned objectives, all of them have been successfully achieved in this project. By using 1-Butyl-3-Methyl Hexafluorophosphate as the ionic liquid and Phenol Red as the dye, it was found out that the adsorption of dye on ionic liquid is possible and the optimum temperature and pH to perform the wastewater treatment is 38.8^{o}C and pH 3.8. This allows the dye removal efficiency to reach at an surprising 95.77% for a regular batch type separation process. It has been observed as well that the phase ratio of ionic liquid to the dye solution does contributes towards the efficiency of dye removal, where by the frequency of contact between the dye and the ionic liquid will be lesser at higher phase ratio causing ineffective adsorption process. Apart from that, concentration of dye also can be seen to affect on the dye removal efficiency, which the limiting active sites of the ionic liquid is unable to adsorb the remaining excess dye molecules, especially at high concentration. Adsorption type has also been confirmed by performing the Langmuir's and Freundlich's Isotherms calculation whereby the adsorption process strongly favors the Langmuir's Isotherm over that of Freunlich's due to the resulting values of the linear regression for both plots.

As mentioned previously in the earlier chapter, textile industry is one of the major polluter to the water resources since it consumes large amount of fresh water as well as the chemicals, dye and organics. Accordingly, the problems that arise such that, the textile manufacturing may produce effluent, which deviate the standards of local legislations. Apart from that, there are varieties of treatment methods in treating the textile effluent. Ionic is preferred compared to the other methods because it is claimed to be versatile in terms of the ionic liquids combination in dealing with different types of dye. Unlike the coagulation and flocculation separation process, adsorption of dye using ionic liquid leaves no potential sludge formation that has risk in endangering the environment.

5.1 Recommendation

The followings are a few recommendations that can be made in order to improve the results obtained and more findings can be made related to this project:

1) "Effect of Types of Ionic Liquid towards Dye Removal" and "Effect of Types of Dye Towards Dye Removal" can be investigated in future for further understanding on the interaction between different types of dyes with different kinds of ionic liquids.

2) "Effect of Dosage of Ionic Liquid towards Dye Removal" may also be carried out to discuss on the effect of amount of ionic liquid towards a fixed volume of dyed waste water so as to determine whether the efficiency of dye removal has any significant increase.

REFERENCES

Absalan, G., Asadi, M., Kamran,S., Sheikhian,L., & Douglas M. (2011). Removal of reactive red-120 and 4-(2-pyridylazo) resorcinol from aqueous samples by Fe_3O_4 magnetic nanoparticles using ionic liquid as modifier. Journal of Hazardous Materials, 192(2), 476-484.

Shahnaz, Q., "Ionic Liquid Mediated Dye Recovery from Aqueous Solution," Nature Precedings, vol. 4, pp. 1-8, 7/23/ 2008.

Al-Degs, Yahya, S., El-Barghouthi, Musa, I., El-Sheikh, Amjad H., & Gavin M. (2008). Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon. Dyes and Pigments, 77(1), 16-23.

Allègre, C., Moulin, P., Maisseu, M., & Charbit, F. (2006). Treatment and reuse of reactive dyeing effluents. Journal of Membrane Science, 269(1–2), 15-34

Baccar, R., Blánquez, P., Bouzid, J., Feki, M., Attiya, H., & Sarrà, M. (2013). Modeling of adsorption isotherms and kinetics of a tannery dye onto an activated carbon prepared from an agricultural by-product. Fuel Processing Technology, 106(0), 408-415.

Chao, P.Y., Wang, J.J., Xuan, X.P., Fan, J., & Fan, M.H. (2007). Factors Affecting Ionic Liquids Based Removal of Anionic Dyes from Water. Environmental Science & Technology, 41(14), 5090-5095

Chen, H.L., Chang, S.K., Lee, C.Y., Chuang, L.L., & Wei, G.T. (2012). Preconcentration of aqueous dyes through phase-transfer liquid-phase microextraction with a room-temperature ionic liquid. Analytica Chimica Acta, 742(0), 54-58

Chen, X.C., Li, F.L., Asumana, C., & Yu, G.R. (2013). Extraction of soluble dyes from aqueous solutions with quaternary ammonium-based ionic liquids. Separation and Purification Technology, 106(0), 105-109

Cho, T.Y., Yoon, S.G., Sekhon,S. S., & Han, C.H. (2011). Effect of Ionic Liquids with Different Cations in I−/I3− Redox Electrolyte on the Performance of Dye-sensitized Solar Cells. Bull. Korean Chem. Soc, 32(6), 2058-2062.

Environment, Department Of. (2009). Guidance Document On The Design And Operation Of Industrial Effluent Treatment Systems (Vol. 5). Malaysia: Environmental Quality (Lndustrial Effluent) Regulations

Kamboh, M.A., Solangi, I.B., Sherazi, S. T. H., & Memon, S. (2011). Synthesis and application of p-tert-butylcalix[8]arene immobilized material for the removal of azo dyes. Journal of Hazardous Materials, 186(1), 651-658

Kusmawati, N., Wijiastuti, A. & Rahmadyanti, E. (2012). Operating Conditions Optimization on“Batik” Dyes Wastewater Treatment by Fenton Oxidation and Separation Using Ultrafiltration Membrane. Journal of Environmental Science & Engineering, 672-682.

Lee, K.E., Morad, N., Teng, T.T., & Poh,B.T. (2012). Effects of Different Conditions on the Removal of Dye from Reactive Dye Wastewater Using Inorganic-Organic Composite Polymer. International Journal of Environmental Science and Development, 3(1), 1-4.

Li, C.P., & Baoping, Xin. (2008). Extraction and Mechanisms of Acid Dyes Into a Room Temperature Ionic Liquid. Paper presented at the Bioinformatics and Biomedical Engineering, 2008.

Malik, A., Hashim, M. A., & Nabi, F.(2011). Ionic liquids in supported liquid membrane technology. Chemical Engineering Journal, 171(1), 242-254.

Maximova, A., & Koumanova, B. (2008). Equilibrium And Kinetics Study Of Adsorption Of Basic Dyes Onto Perfil From Aqueous Solutions. Journal of the University of Chemical Technology and Metallurgy, 43(1), 101-108.

Merzouk, B., Yakoubi, M., Zongo, I., Leclerc, J. P., Paternotte, G., Pontvianne, S., & Lapicque, F. (2011). Effect of modification of textile wastewater composition on electrocoagulation efficiency. Desalination, 275(1–3), 181-186

Misuk, V., Breuch, D., & Löwe, H. (2011). Paramagnetic ionic liquids as “liquid fixed-bed” catalysts in flow application. Chemical Engineering Journal, 173(2), 536-540.

Moghaddam, S. S. , Alavi M.R. , & Arami, M . (2010). Decolorization Of An Acidic Dye From Synthetic Wastewater By Sludge Of Water Treatment Plant. *7*(5), 437-442

Othman, N., Mili, N., Zailani, S.N., & Mohammad, N.A.B. (2010). Extraction Of Remazol Brilliant Orange 3R From Textile Wastewater Using Tetrabutyl Ammonium Bromide. Jurnal Teknologi, 53(4), 29–39.

Othman, N., Mili, N., & Wong, Y.M. (2011). Liquid-liquid Extraction of Black B Dye from Liquid Waste Solution Using Tridodecylamine. Journal of Environmental Science and Technology, 4(3), 324-331

Othman, N., Zailani, S. N., & Mili, N. (2011). Recovery of synthetic dye from simulated wastewater using emulsion liquid membrane process containing tri-dodecyl amine as a mobile carrier. Journal of Hazardous Materials, 198(0), 103-112

Pandit, P, & Basu, S. (2004). Removal of Ionic Dyes from Water by Solvent Extraction Using Reverse Micelles. Environmental Science & Technology, 38(8), 2435-2440

Qadri, H., Ashley, G. and Yousef, H. (2008). Ionic Liquid Mediated Dye Recovery from Aqueous Solution. *Nature Precedings*, *4*(2), 1-8

Rajamohan, N. (2009). Equilibrium studies on sorption of an anionic dye onto acid activated water hyacinth roots. African Journal of Environmental Science and Technology, 3(11), 399-404.

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology, 77(3), 247-255.

Salleh, M. A. M., Mahmoud, D.K., Karim, W.A., Wan, A., & Idris, A., (2011). Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination, 280(1–3), 1-13

Shakir, K., Elka, F., Ahmed , F., Ghoneimy, H.F., Elrab B., Shokry G., & Refaat, M. (2010). Removal of rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater simulants by ion flotation. Water Research, 44(5), 1449-1461

Tehrani-Bagha, A.R., Nikkar,H., Mahmoodi, N.M, Markazi, M., & Menger, F.M., "The sorption of cationic dyes onto kaolin: Kinetic, isotherm and thermodynamic studies," Desalination, vol. 266, pp. 274-280, 1/31/ 2011.

Vijayaraghavan, R., Vedaraman, N., Surianarayanan, M., & MacFarlane, D. R. (2006). Extraction and recovery of azo dyes into an ionic liquid. Talanta, 69(5), 1059-1062.

Zouboulis, N. D. Tzoupanos And A. I. (2008). Coagulation-Flocculation Processes In Water/Wastewater Treatment: The Application Of New Generation Of Chemical Reagents. 6th IASME/WSEAS International Conference On Heat Transfer, Thermal Engineering And Environment, 3(2), 309-318.

APPENDICES

References	Affiliation	Findings
Chao Pei, Y et al. (2007)	Lanzhou University, Lanzhou	-The % of dye removal varies with: 1)Temperature 2)Phase volume ratio, pH 3)Salt concentration in wastewater 4)Chemical structure of ILs
Changping, L.(2008)	Dalian University, China	- Removal of Acid Yellow RN with room temperature ionic liquid (1-butyl-3-Methylimidazolium Hexafluorophosphate). - Removal of Acid Brilliant Red B with room temperature ionic liquid (1-butyl-3-Methylimidazolium Hexafluorophosphate).

References	Affiliation	Findings
Moghaddam, S et al. (2010)	AUT, Tehran	- Coagulation/flocculation of solutions containing an acidic dye proved that reusing water treatment plant sludge as a coagulating agent in acid red 119 dye removal to be effective.
Kamboh, A.M et al (2011)	University of Sindh, Pakistan	- The sorption trend was found to follow Langmuir isotherm model as compared to the Freundlich isotherm - p-tert-butylcalix[8]arene has high capacity to absorb RB-5 and RR-45 azo dyes from the contaminated wastewater.
Merzouk, B et al. (2011)	University of Mohamed	- Turbidity and TOC were shown to be additive variables in the treatment of the dye solution and the industrial textile waste - Electrocoagulation seems to proceed with no interaction between the dye stuff as well as the coagulant used.

References	Affiliation	Findings
Cengiz Sevilay et al (2011)	Akdeniz University, Turkey	- The maximum adsorption capacity of P. oceanica was found to be 68.97 mg/g at 25 ◦C. - This waste material may be a suitable adsorbent for decolorization of industrial effluents due to its low cost and sufficient adsorption
El-Mekkawi, D.M et al (2011)	NRC Dokki, Egypt	- The main photodegradation of B2RL takes place at the surface of the catalyst. - Possibility of using rutile TiO_2 in treatment of wastewater containing B2RL
Menezes, E.W et al (2012)	University of Campinas, Brazil	- The maximum adsorption capacities were 165.4, 190.3 and 195.9 mg g^{-1} for Py/Si-90, Py/Si-92 and Py/Si-94, respectively - the sample Py/Si-94, which presents higher specific surface area, higher pore volume and also higher pore diameter, shows the best results.

References	Affiliation	Findings
Kumar, A.S et al (2012)	CCS University, India	- Strains of *Aspergillus* are capable of degrading textile dye. -19 *Aspergillus* strains were isolated and tested against dye degradation and found to have good results.
Lee et al. (2012)	USM, Penang	- At temperature above 30^{o}C of dyed wastewater, reduction in % of dye removal was observed. - Effect of dosage on the dye removal (%) was studied with respect to concentration of dye. -The dye removal (%) was found increase to a maximum value of 99% and decrease thereafter.